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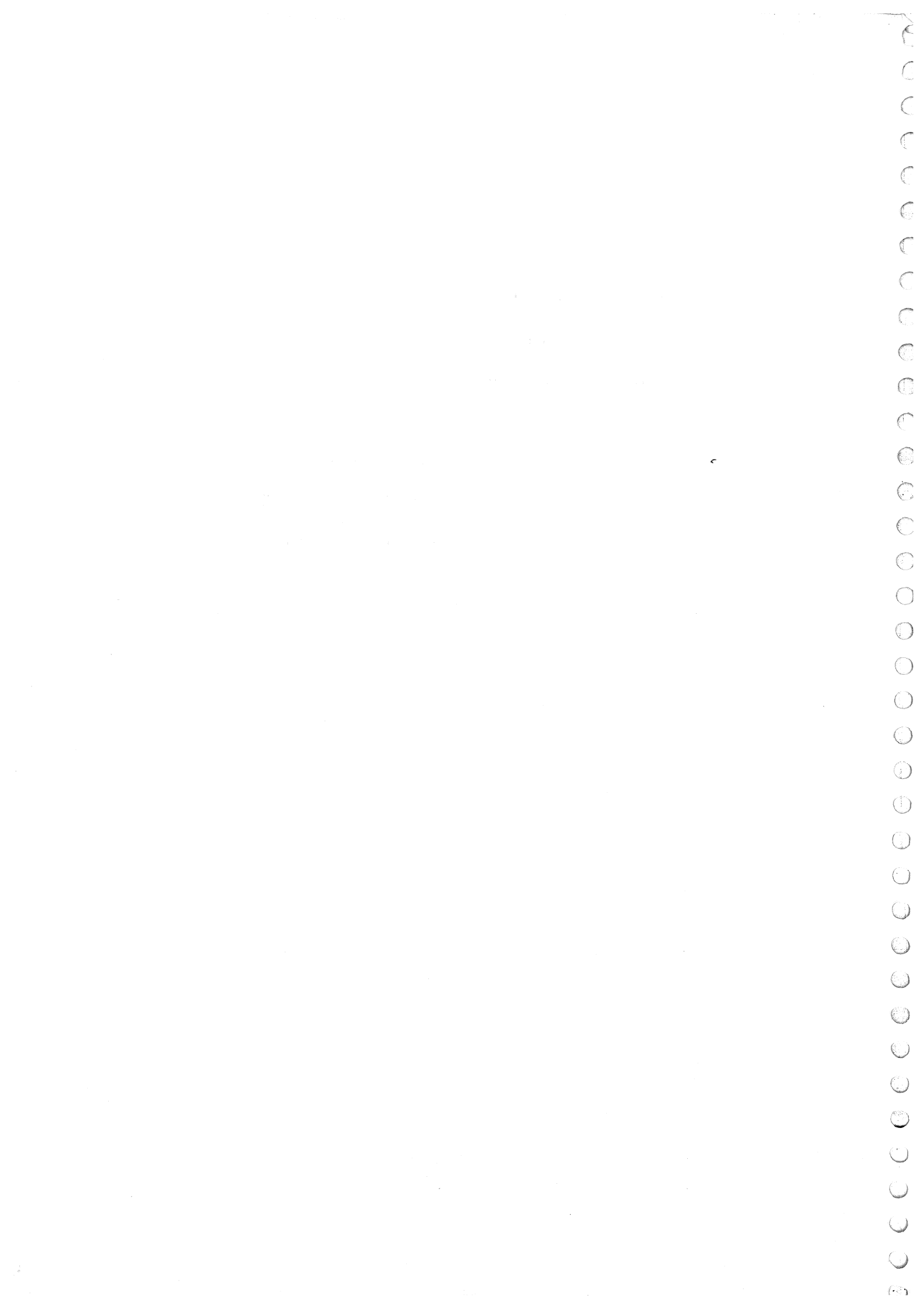
CSIR NET-JRF

Physical Chemistry

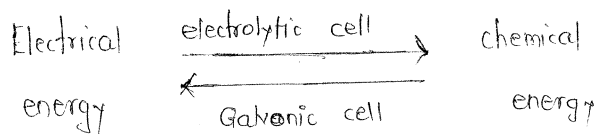
→ Electrochemistry - 8/10 marks

→ Chemical equilibrium - 6/8 marks

→ Chemical kinetics. - 8/10 marks



# ☆ ELECTROCHEMISTRY ☆



→ conductor : allows passage of current through it

(i) electronic / metallic conductor : flow of electrons

(ii) electrolytic conductors : flow of ions

(i) electronic conductors

→ conductivity due to flow of electrons.

Ex - metal

→ No chemical changes takes place.

☆ →  $T \uparrow \rightarrow$  mobility of  $e^- \downarrow$  due to collision between moving electrons and lattice vibration (phonons)

→ conductivity  $\downarrow$ .  
→ No flow of matter occurs.

(ii) electrolytic conductor

→ conductivity due to flow of ions in aqueous state or molten state

Ex :  $\text{NaCl} + \text{H}_2\text{O} \rightarrow$  } conduct electricity  
           molten NaCl  $\rightarrow$  }

→ conductivity is due to flow of ions.

Ex : strong acid

      strong base

      salts

→ Chemical changes occurs.

→ flow of matter takes place

→  $T \uparrow \rightarrow$  mobility of ions increases  $\neq$  hence conductivity increases  $\uparrow$

## electrolytic conductors

← strong electrolytes

(d) degree of ionization is high.

Ex -  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{NaCl}$

← weak electrolytes

degree of ionization is low

Ex -  $\text{CH}_3\text{COOH}$ ,  $\text{HCN}$ ,  $\text{NH}_4\text{OH}$

## strong electrolytes

→ degree of ionization ( $\alpha$ ) is high

→ ~~mob~~ no. of ions high & mobility of ions is high

→ conductivity ~~to~~ is high.

→ ~~ex~~ HCl, H<sub>2</sub>SO<sub>4</sub>, NaOH, KOH, NaCl, KCl } degree of ionization =  $\frac{\text{no. of molecules ionized}}{\text{total no. of molecules}}$

## weak electrolyte

→ degree of ionization ( $\alpha$ ) - low

→ no. of ions - low & hence mobility of ions - low

→ conductivity - low

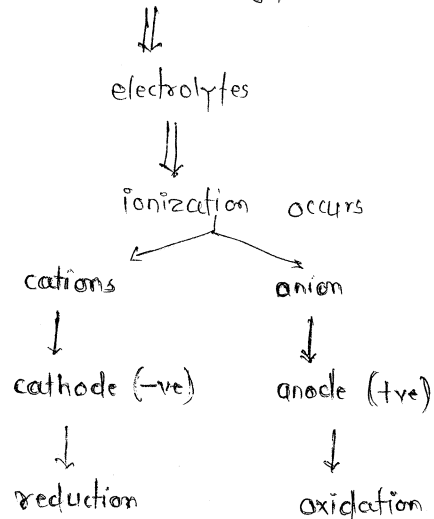
→ CH<sub>3</sub>COOH, HCN, BaSO<sub>4</sub>, PbSO<sub>4</sub>

# Non-conductor/insulator : donot allow ~~ee~~ current to flow through it.

Es : diamond, plastic.

## # Electrolysis

⇒ electrical energy → chemical energy



tricks

LOGR

ReCaOxAn

Gal at Ca +ve terminal

⇒ condition for operating electrolytic cell :

:  $\Delta G > 0$  ,  $\Delta E < 0$

⇒ electrolytic cell

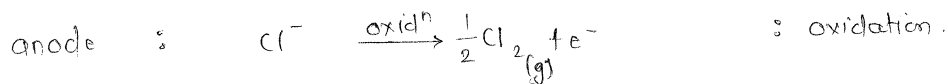
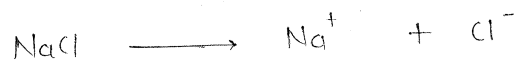
⇒  $\Delta G = +ve$  ,  $E = -ve$  ∴  $\Delta G = -nFE$

## Electrolysis using ~~inter~~ inert electrode

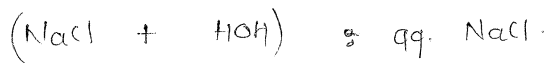
inert electrode : graphite / Pt



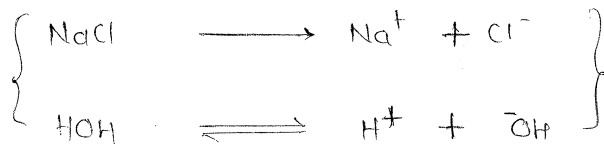
(a) electrolysis of molten NaCl



(b) electrolysis of aqueous NaCl.

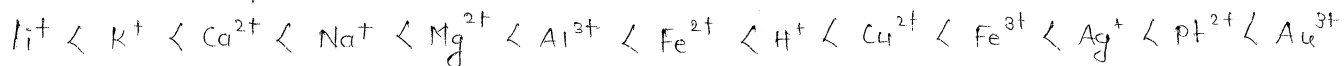


dielectric constant : it is measure of weakening of attraction between cation & anion.



reduction of  $\text{Na}^+$  &  $\text{H}^+$  depends on reduction potential.

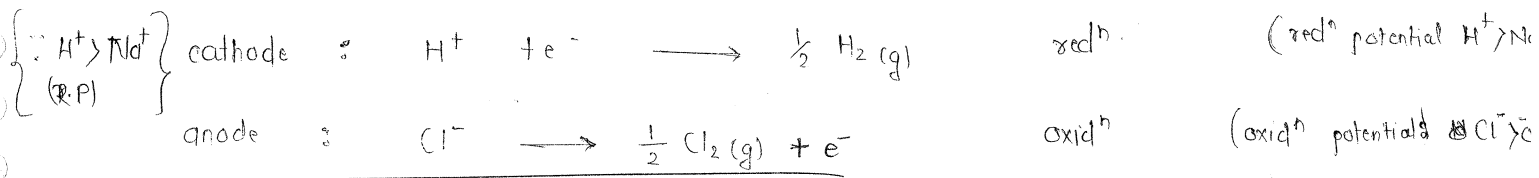
→ order of reduction potential of cation



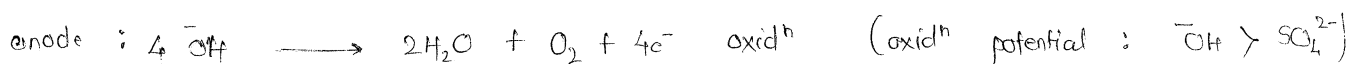
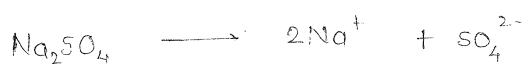
→ order of reduction potential of anion



→ order of oxidation potential of anion



Example ① aq.  $\text{Na}_2\text{SO}_4$



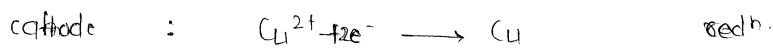
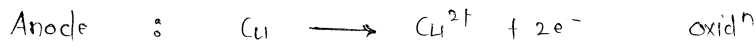
~~Example 1~~ ~~अप-वाहन~~

- ज्या cation चें Reduction potential जास्त तो सर्वात आधी reduction दाखवतो
- ज्या anion चें oxidation potential जास्त तो सर्वात आधी oxidation दाखवतो
- oxidation potential = - reduction potential

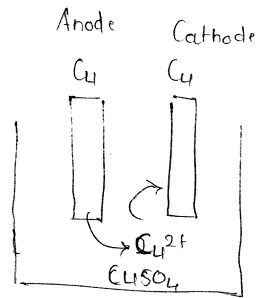
II) Electrolysis using aqueous active electrode :

active electrode : Cu / Ag / Au

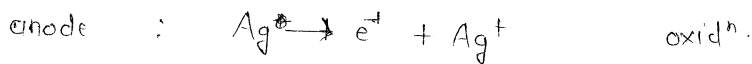
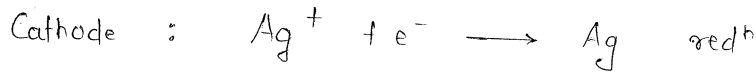
Ex : Electrolysis of  $\text{CuSO}_4$  by using Cu electrode :



net change : migration of : Cu from anode to cathode.

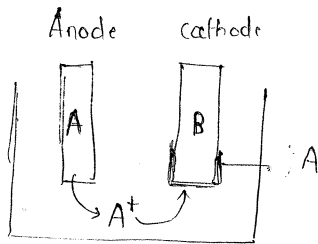


Example 2 Electrolysis of  $\text{AgNO}_3$  using Ag electrode.



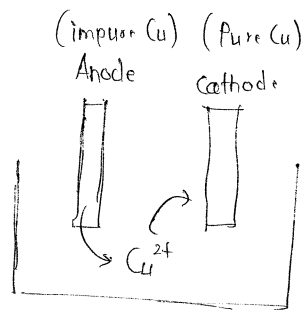
net change : migration of Ag from anode  $\longrightarrow$  cathode.

$\longrightarrow$  This phenomenon is useful in electroplating and electrorefining.



electroplating

↓  
used to reduce  
corrosion of metal  
B



electrorefining

↓  
{ impure metal  $\longrightarrow$  pure metal }

trick :  $\longrightarrow$  more oxid<sup>n</sup> potential having anion oxidizes first at anode.

$\longrightarrow$  more red<sup>n</sup> potential having cation reduces at cathode

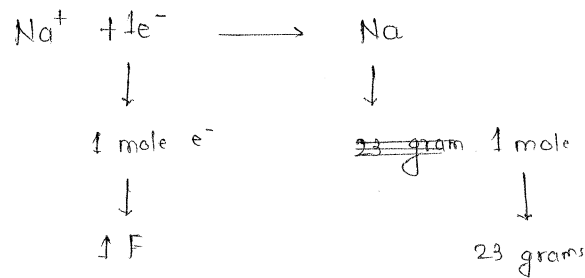
$$1 F = 6 \times 10^{23} \text{ number of electron. } \times 1.602 \times 10^{-19} \text{ C.}$$

$$1 F = 96,500 \text{ C}$$

→ by passing 1F current, 1 gram eq. of substance will be deposited.

Ex :  $\text{Na}^+$  : Eq. wt =  $\frac{\text{molar mass}}{\text{valency}} = \frac{23}{1} = 23 \text{ gm. eq.}$

1 F current → 23 gram of Na is deposited at cathode.

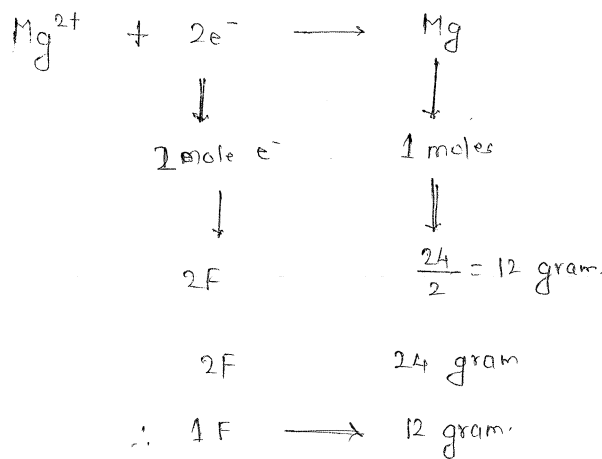


By passing 1F current, 23 gram of Na is deposited at cathode.

Eq. wt =  $\frac{\text{molar mass}}{\text{valency}}$   
unit = gm. eq.

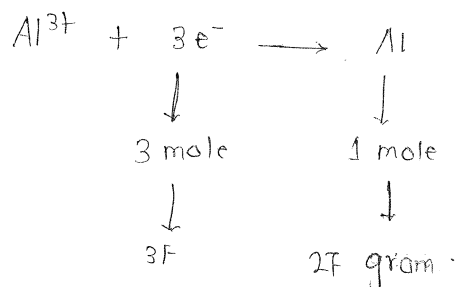
Example :  $\text{Mg}^{2+}$  ∴ Eq. wt =  $\frac{24}{2} = 12 \text{ gram.}$

1 F → 12 grams of Mg is deposited at cathode.



Example ③ :  $\text{Al}^{3+}$ .

equ. wt =  $\frac{\text{molar mass}}{\text{valency}} = \frac{27}{3} = 9 \text{ grams.}$



$x = \frac{1}{3} \text{ mole.}$

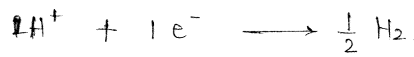
∴ 1F x

1F - current → deposits 9 gram of  $\text{Al}^{3+}$  at cathode.

$x = \frac{27}{3} = 9$

Example (4)  $H^+$  : Eq. wt =  $\frac{1}{1} = 1$  gram

1 F  $\longrightarrow$  1 gram of  $H_2$  gas is evolved.



1 F  $\longrightarrow$   $\frac{1}{2}$  mole  $H_2$  evolved at cathode

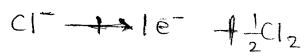
$\longrightarrow$  11.2 L of  $H_2$  is evolved.

at STP :  $V_{eq} = 11.2$  L.

We must have to learn electrolysis of  $H_2O$  which is present in latter part of notebook.

Example (5)  $Cl^-$  : eq. wt =  $\frac{35.5}{1} = 35.5$ .

1 F  $\longrightarrow$  35.5 gram of  $Cl_2$  evolved at anode.



1 F  $\longrightarrow$   $\frac{1}{2}$  mole of  $Cl_2$  is evolved

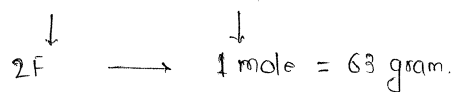
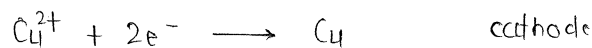
$\longrightarrow$  11.2 L of  $Cl_2$  is evolved.

$V_{eq}(Cl_2) = 11.2$  L.

Example 6 :  $Cu^{2+}$

eq. wt =  $\frac{63}{2} = 31.5$  grams

1 F current is required to deposit 31.5 grams of  $Cu^{2+}$  at cathode



$\therefore$  1 F  $\longrightarrow$  31.5 grams

Note : (i) To deposit univalent 1 mole cation : 1 mole of electron required  
: 1 F current is required

(ii) To deposit 1 mole of bivalent cation : 2 mole of  $e^-$  required  
: 2 F current is required.

(iii) To deposit 1 mol of trivalent cation : 3 moles of  $e^-$  required  
: 3 F current is required.

(iv) To deposit 1 gram. eq. of uni/bi/trivalent cation : 1 F is required.

## # Faraday 1<sup>st</sup> law of electrolysis.

proportional to the quantity of current (electric charge) passed through the electrolytic solution.

$$W \propto Q$$

$$W \propto Q$$

W - Amount of substance deposited at electrode

Q = charge.

$$W \propto It$$

I - current t = time

$$W = ZIt$$

$$\therefore Q = It$$

Z - electrochemical equivalent.

→ 1 F (96,500 C) passed : 1 gram eq. substance deposited Eq. wt

2F (2 × 96,500) C passed : 2 gram. eq. substance deposited W

Q Coloumb passed : W.

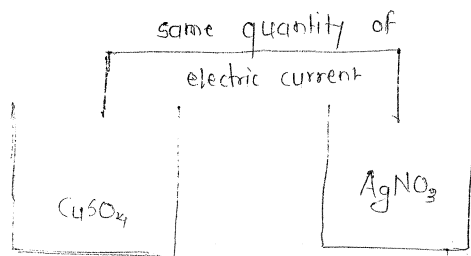
$$W = \frac{Q \times \text{Eq. wt}}{F} = \frac{\text{Eq. wt} \times It}{F}$$

For gases

$$W = \frac{V_{\text{eq.}} Q}{F} = \frac{V_{\text{eq.}} It}{F}$$

$$\rightarrow Z = \frac{W}{Q} = \frac{W}{It} \quad \text{Unit : gm/C or gm/A.sec}$$

## # Faraday's 2<sup>nd</sup> law of electrolysis.



$$1F \quad \text{Eq. wt} = \frac{63.5}{2} = 31.7 \text{ gr} \quad \text{Eq. wt} = \frac{108}{1} = 108 \text{ gr} \quad \Rightarrow \quad 31.7 : 108$$

$$2F \quad \text{Eq. wt} = 31.7 \times 2 \text{ gm} \quad \text{Eq. wt} = 108 \times 2 \text{ gm} \quad \Rightarrow \quad 2 \times 31.7 : 2 \times 108 \text{ gm}$$

$$\frac{W_1}{W_2} = \frac{\text{Eq. wt } 1}{\text{Eq. wt } 2}$$

When same quantity of electric current is passed through different electrolyte solution, the ratio of amount/wt. of substance deposited at electrode is in the ratio of their equivalent wt.

$$\frac{W_1}{W_2} = \frac{\text{eq. wt } 1}{\text{eq. wt } 2}$$

# Resistance (R) : obstruction to the flow of current is called resistance

$$R \propto \frac{l}{a}$$

$l$  - length of electrode.

$a$  - area of electrode / area of cross-section

$$R = \rho \cdot \frac{l}{a}$$

$\rho$  - resistivity / specific resistance

↓

$$\because l = 1 \text{ cm}$$

$$a = 1 \text{ cm}^2 \Rightarrow V = 1 \text{ cm}^3$$

$$R = \rho \frac{l}{a} \Rightarrow R = \rho$$

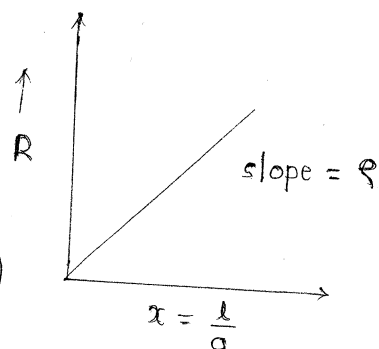
→ specific resistance,  $\rho$  : resistance shown by 1 cm<sup>3</sup> conductor or 1 ml electrolytic solution.

$$\rho = \frac{R \cdot a}{l} = \frac{\Omega \cdot \text{cm}^2}{\text{cm}} = \Omega \cdot \text{cm}$$

$$\text{unit} = \Omega \cdot \text{cm}$$

$$R = \rho \cdot x$$

$$y = mx + (c=0)$$



# Conductance (C) : Reciprocal of resistance.

$$C = \frac{1}{R}$$

$$C = \frac{1}{\rho} \cdot \frac{a}{l}$$

$$C = K \cdot \frac{a}{l}$$

$K$  - specific conductance / conductivity

$$K = \frac{1}{\rho} =$$

$$C = \frac{1}{\rho} \cdot \frac{a}{l} = K \cdot \frac{a}{l}$$

→  $K = \frac{C \cdot a}{\rho}$  : conductance shown by 1 cm<sup>3</sup> conductor / 1 ml of electrolyte solution

if  $a = 1 \text{ cm}^2 \implies V = 1 \text{ cm}^3 \quad l = 1 \text{ cm}$

then  $K = C$

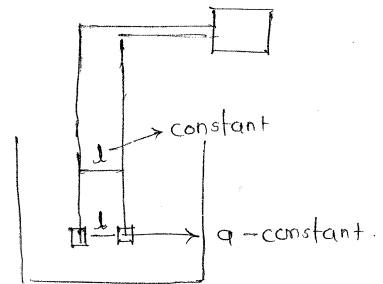
→ unit  $K = \frac{1}{\rho} = \frac{1}{\Omega \cdot \text{cm}} = \Omega^{-1} \cdot \text{cm}^{-1}$

$$K_{\text{unit}} : \Omega^{-1} \text{cm}^{-1}$$

# Cell constant ( $\alpha$ ) : For a given conductivity cell  $l$  &  $a$  are constant so their ratio  $\frac{l}{a}$  is also a constant which is called cell constant  $\alpha$

$$\alpha = \frac{l}{a}$$

$$\alpha_{\text{unit}} = \text{cm}^{-1}$$



→  $R = \rho \cdot \frac{l}{a} \quad \therefore R = \rho \cdot \alpha$

→  $C = K \frac{a}{l} \quad \therefore C = \frac{K}{\alpha}$

$$K = \alpha \cdot C$$

K - specific conductance

$\alpha$  - cell constant

C - conductance

# molar conductance ( $\Lambda_c / \lambda_m$ ) : The conductance of solution containing 1 mole of electrolyte is called molar conductance ( $\Lambda_c / \lambda_m$ )

cond<sup>n</sup> — 1 mole of electrolyte

$$1 \text{ ml} = K$$

$$2 \text{ ml} = 2K$$

for V ml volume  $V \text{ ml} = VK$

$$\Lambda_c = K \cdot V (\text{in ml})$$

$$\text{conc. } C_M = \frac{n=1}{V(\text{in ml.})} \times 1000$$

$$V(\text{in ml.}) = \frac{1000}{C_M}$$

$C_M$  - molar concentration.

$C_M$  - conc. in molarity.

$$\therefore \boxed{\kappa_c = \frac{1000 K}{C_M}}$$

(ml = cm<sup>3</sup>)

Unit :  $\Omega^{-1} \text{ cm}^{-1} \text{ mol}^{-1} \cdot \text{cm}^3$  or  $\text{mho} \cdot \text{cm}^{-1} \cdot \text{mol}^{-1} \cdot \text{ml}$

:  $\Omega^{-1} \text{ cm}^2 \cdot \text{mol}^{-1}$  or  $\text{mho} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ .

### # equivalent conductance ( $\lambda_c$ )

cond<sup>n</sup> - 1 gram. eq. of electrolyte.

$$1 \text{ ml} = K$$

$$2 \text{ ml} = 2K$$

$$V \text{ ml} = VK$$

$$\boxed{\lambda_c = K \cdot V(\text{in ml})}$$

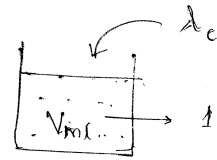
$$C_N = \frac{n_{\text{gm. eq.}} = 1}{V(\text{in ml})} \times 1000$$

$$V(\text{in ml}) = \frac{1000}{C_N}$$

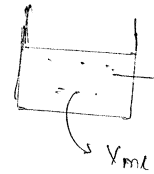
$C_N$  = Normality conc.

$$\boxed{\lambda_c = \frac{K \times 1000}{C_N}}$$

Unit :  $\Omega^{-1} \cdot \text{cm}^{-1} \text{ cm}^3 \cdot \text{gm. eq.}^{-1}$  or  $\Omega^{-1} \cdot \text{cm}^2 \cdot \text{gm. eq.}^{-1}$ .



1 gm. eq. NaOH  
= 40 gm NaOH



1 gm. eq. H<sub>2</sub>SO<sub>4</sub> =  $\frac{98}{2}$   
= 49 gram.

### # relation between $\kappa_c$ & $\lambda_c$ .

$$\lambda_c = \frac{1000 K}{C_N}$$

Normality  $C_N \equiv$  molarity  $C_M \times$  valency  $Z$

$$\lambda_c = \frac{1000 K}{C_M \times Z}$$

$Z$  - valency.

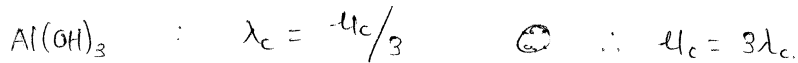
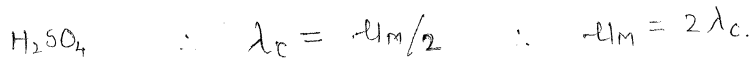
$$\boxed{\lambda_c = \frac{\kappa_c}{Z}}$$

$\lambda_c$  - equivalent conductance

$\kappa_c$  - molar conductance

$Z$  - valency





# transport number - Fraction of current carried by an ion to the total current is

called transport number:

$A^+ \quad B^-$

→ current carried by ion  $\propto$  it's velocity ( $v$ )

total current = 100 unit

cation = 60 unit

anion = 40 unit.

transport no. of cation =  $\frac{60}{100} = 0.6$

transport no. of anion =  $\frac{40}{100} = 0.4$

→ transport number of (cation + anion) = 1

→ transport number of cation =  $\frac{\text{current carried by cation}}{\text{total current}} = \frac{V_c}{V_c + V_a}$

transport number of anion =  $\frac{\text{current carried by anion}}{\text{total current}} = \frac{V_a}{V_c + V_a}$

→  $t_+ + t_- = 1$  i.e. the sum of transport number of cations and anions in an electrolyte is always equal to 1.

# Effect of dilution on conductance :

→ dilution : addition of solvent

→ on dilution  $\Rightarrow$  degree of ionization  $\alpha \uparrow \Rightarrow$  no. of ions  $\uparrow$

↓

specific conductance,  $K$  decreases  $\downarrow$

since no. of ions present in 1 ml / 1 cm<sup>3</sup> decreases on dilution.

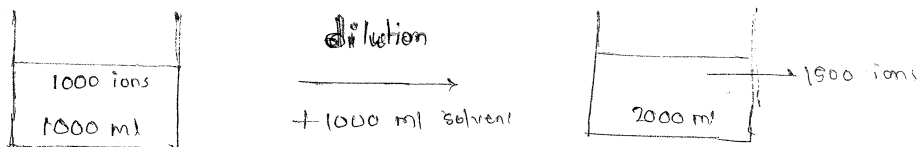
↓

conductance  $\uparrow$

↓

both  $\mu_c$  &  $\lambda_c \uparrow$  with dilution as Volume in ml increases

Ex



$\mu_c \uparrow$  but  $K \downarrow$

$\lambda_c \uparrow$

## (I) strong electrolytes

→ At high conc.  $\Rightarrow$  100% ionization.

→ on dilution  $\Rightarrow$  degree of ionization remains constant.

$\Downarrow$   
conductance  $\uparrow$  increases slowly

due to increase in mobility of ions and reaches a max. value at  $\infty$  dilution or zero conc. which is called equivalent conductance at  $\infty$  dilution or zero conc. ( $\lambda_{\infty}/\lambda_0$ )

1 M	→	100 unit conductance.
0.5 M	→	110 unit
0.1 M	→	120 unit
0.01 M	→	130 unit
0.0001 M	→	135 unit
0.0000001 M	→	135 unit

} reached a max. value of conductance.

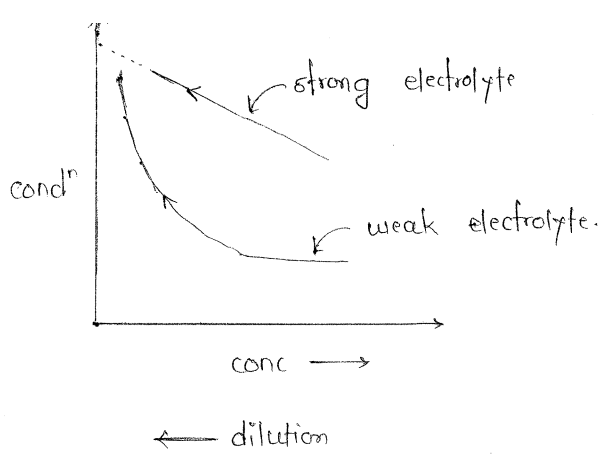
## (II) Weak electrolytes

→ At high conc.  $\Rightarrow$  degree of ionization is low

→ on dilution  $\Rightarrow$  degree of ionization  $\uparrow$   $\Rightarrow$  no. of ions  $\uparrow$

$\Downarrow$   
conductance  $\uparrow$  sharply but

even at high dilution doesn't reach a max. / constant value. So it is not possible to determine  $\lambda_{\infty}/\lambda_0$  experimentally.



possible to calculate equivalent conductance at  $\infty$  dilution or zero conc. for  $(\lambda_{\infty}/\lambda_0)$  for weak electrolyte experimentally but can be obtained for strong electrolyte by extrapolation.

→  $\alpha$ , degree of ionization =  $\frac{\lambda_c}{\lambda_{\infty}}$

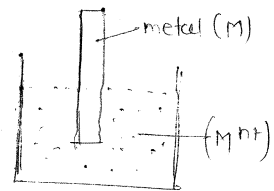
conc.	100 molecules		conductance
	molecule	ions	
10 M	90	10	100 unit
5 M	80	20	200 unit
1 M	60	40	400 unit
⋮			
0 M	1	100 ions	1000 unit. = $\lambda_{\infty}$

$$\alpha = \frac{\lambda_c}{\lambda_{\infty}}$$

# Electrode potential: Tendency to loose or gain electron is called electrode potential.

tendency to loose electron: oxid<sup>n</sup> potential.

tendency to gain electron: red<sup>n</sup> potential



- electrode potential depends on
- (i) nature of metal electrode
  - (ii) temperature
  - (iii) conc.

When a metal is placed in the solution having its ions, metal gets either +ve or -ve charge with respect to solution, so called electrode potential difference is developed between metal and its solution is called electrode potential.

→ oxid<sup>n</sup> potential = - red<sup>n</sup> potential  
 $\Delta.P = - R.P.$

# Standard Electrode potential ( $E^\circ$ ) — The electrode potential measured at  $25^\circ\text{C}$  temp &  $1\text{M}$  conc. of electrolytic solution is called standard electrode potential.

→ condition temp :  $25^\circ\text{C}$   
 $C : 1\text{M}$ .

→  $E^\circ$  depends on only

(i) Nature of metal  $\because T = \text{constant}$  &  $C = 1\text{M}$  (constant).

→  $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34\text{V}$  — standard reduct<sup>n</sup> potential

$E^\circ(\text{Cu}/\text{Cu}^{2+}) = -0.34\text{V}$  — standard oxid<sup>n</sup> potential.

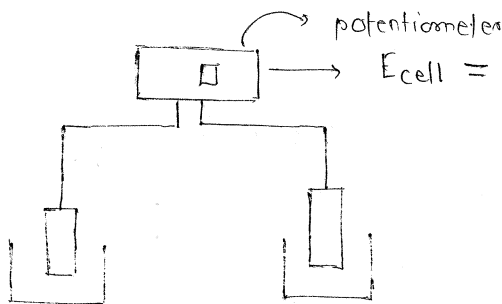
→  $E^\circ(\text{Ag}^+/\text{Ag}) = +0.80\text{V}$  — S.R.P

$E^\circ(\text{Ag}/\text{Ag}^+) = -0.80\text{V}$  — S.O.P.

→  $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76\text{V}$  — S.R.P

$E^\circ(\text{Zn}/\text{Zn}^{2+}) = +0.76\text{V}$  — S.O.P.

→ It is not possible to determine single electrode potential experimentally but the difference between two electrode potential which is called cell potential / cell E.M.F ( $E_{\text{cell}}$ ) can be determined experimentally by using potentiometer.



— determined experimentally.

→  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$  (red<sup>n</sup> potential)

→  $E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}}$  (oxid<sup>n</sup> potential)

→  $E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$   
 (R.P) (O.P)

→ single electrode potential can be determined by using reference electrode whose electrode potential is known to us.

Ex : standard Hydrogen electrode , saturated calomel electrode.

$$E_{H_2}^{\circ} = 0$$

$$E_{H_2/H^+}^{\circ} = E_{H^+/H_2}^{\circ} = 0$$

Anode : reduction potential of  $H^+ < M^{n+}$

cathode : reduction potential of  $H^+ > M^{n+}$

### (i) standard hydrogen electrode.

→ E.P = 0

→ 1<sup>o</sup> reference electrode

Anode :  $H_2 \longrightarrow 2H^+ + 2e^-$  oxid<sup>n</sup>.

Cathode :  $2H^+ + 2e^- \longrightarrow H_2$  red<sup>n</sup>.

→ representation : (i) When acting as anode :  $Pt(s), H_2(g) | H^+(aq) (1M)$

(ii) When acting as cathode :  $H^+(aq, 1M) | H_2(g, 1atm), Pt(s)$

#### reference electrode.

→ Standard Hydrogen Electrode  
- 1<sup>o</sup> reference electrode

→ Standard Calomel Electrode  
- 2<sup>o</sup> reference electrode

### (ii) standard calomel electrode.

→ electrode potential : 0.242 V.

→ Hg, Hg<sub>2</sub>Cl<sub>2</sub> , saturated KCl, Pt

↳ metal-metal insoluble salt electrode.

Anode :  $2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-$  (oxid<sup>n</sup>)

Cathode :  $Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-$  (red<sup>n</sup>)

→ secondary reference electrode

→ representation (i) when acting as anode :  $Pt, Hg-Hg_2Cl_2 | KCl (sat)$

(ii) when acting as cathode :  $KCl (sat) || Pt, Hg-Hg_2Cl_2$

### # Cell notation / cell representation.

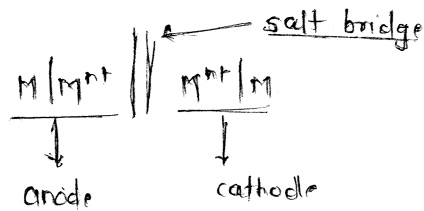
→ salt bridge : //

→ no salt bridge : ;

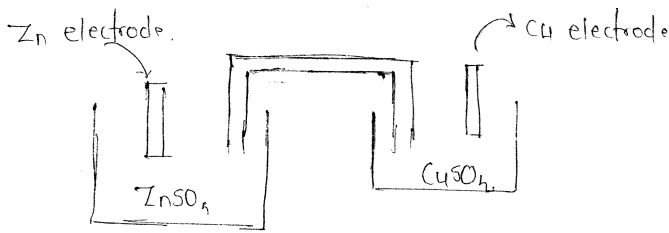
→ left side of salt bridge : anode  $M | M^{n+}$  metal followed by metal ion

→ right side of salt bridge : cathode  $M^{n+} | M$  red<sup>n</sup>

→ cell representation



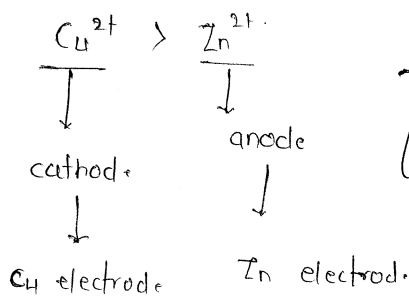
Ex: Daniel cell : Zn & Cu electrode.



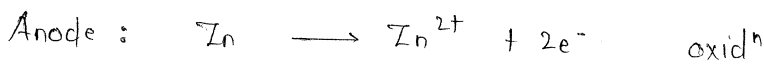
R.P. more → acts as cathode

R.P. less → acts as anode

R.P. order.



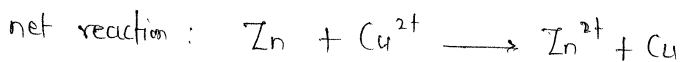
ज्याच R.P. जास्त तो metal  
cathode साखवा किंवा cathode  
होऊन वापरला जातो



$$E_{\text{Zn}/\text{Zn}^{2+}}^{\circ} : -0.76 \text{ V}$$



$$E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} : +0.34 \text{ V}$$



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \quad (\text{R.P.})$$

$$= 0.34 - (-0.76 \text{ V})$$

$$= 1.1 \text{ eV.}$$

### ★ IMPORTANT FORMULAE ★

→  $W \propto Q$

$$W = \frac{ZIt}{F}$$

→  $\lambda_c = KV = \frac{1000K}{C_m}$

→  $W_1 : W_2 = \text{Eq. wt } 1 : \text{Eq. wt } 2$

→  $\lambda_c = \frac{e_c}{z}$

→  $e_c = K.V = \frac{1000K}{C_m}$

→  $e_c = z \times \lambda_c$

→  $R = \rho \cdot \frac{l}{a} = \rho \cdot x$

→  $C = \frac{1}{R} = \frac{1}{\rho} \cdot \frac{a}{l} = K \cdot \frac{a}{l} = \frac{K}{x}$

$$\rightarrow K = c \cdot x$$

total current

$$\rightarrow t_- = \frac{\text{current carried by anion}}{\text{total current}}$$

$$\rightarrow t_+ + t_- = 1$$

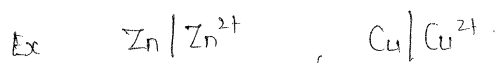
$$\rightarrow E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (\text{red}^n \text{ potential})$$

$$E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}} \quad (\text{oxid}^n \text{ potential})$$

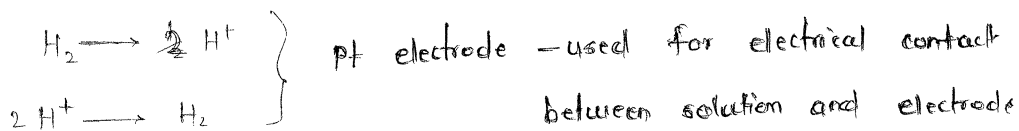
$$E_{\text{cell}} = E_{\text{cathode}} (\text{R.P}) + E_{\text{anode}} (\text{O.P})$$

## # Types of electrode

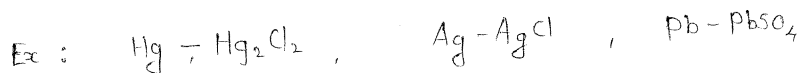
(i) Metal-metal ion electrode :  $M/M^{n+}$



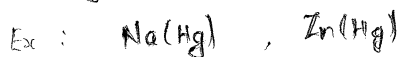
(ii) Gas electrode :  $H_2, Cl_2$



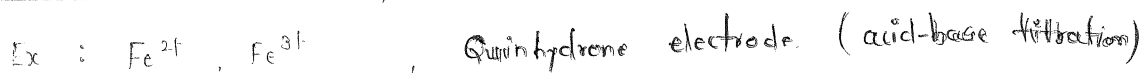
(iii) metal-metal insoluble salt electrodes



(iv) metal-amalgam electrode



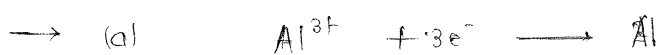
(v) redox electrodes :  $Fe^{2+}, Fe^{3+}$



Que-1 How much charge in Coulombs required to reduce

(a) 1 mole of  $Al^{3+}$  to  $Al$

(2) 1 mole of  $MnO_4^-$  to  $Mn^{2+}$



$$\downarrow$$

$$3F = 3 \times 96,500 \text{ C} = 289,500 \text{ C}$$

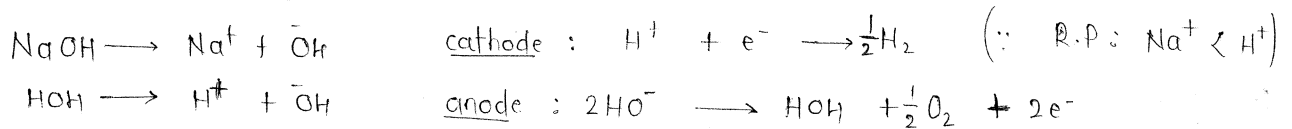


$$\downarrow$$

$$5F = 5 \times 96,500 \text{ C} = 482,500 \text{ C}$$

Que-2 Electrolysis of aqueous solution of 1 M NaOH results in.

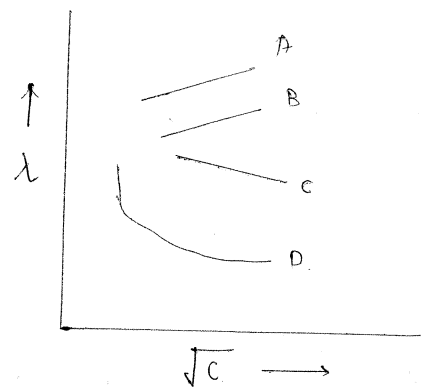
- (i) Na at cathode & O<sub>2</sub> at anode.
- (ii) H<sub>2</sub> at cathode & O<sub>2</sub> at anode
- (iii) Na, H<sub>2</sub> at cathode & O<sub>2</sub> at anode.
- (iv) O<sub>2</sub> at cathode & H<sub>2</sub> at anode



$\therefore$  option (ii) is the correct answer.

Que-3 The graph, the correct option is

- (i) A : weak electrolyte & B : strong electrolyte.
- (ii) C : strong electrolyte & D : weak electrolyte
- (iii) A : strong electrolyte & B : strong electrolyte
- (iv) C : weak electrolyte & D : strong electrolyte



$\rightarrow$  A/c Kohlrausch's law, for strong electrolyte  $\lambda_m = \lambda_m^\infty - k\sqrt{C}$ .

on dilution  $\Rightarrow$  for strong electrolyte,  $\lambda$   $\uparrow$  slowly & become steady

for weak electrolyte,  $\lambda$   $\uparrow$  sharply & don't reaches max. value

$\therefore$  option (iii) is

correct answer

Que-4 When same quantity of current is passed through CuSO<sub>4</sub>, AgNO<sub>3</sub>, if 3.175 gm

of Cu is deposited, the weight of silver deposited is

$$\frac{w_1}{w_2} = \frac{\text{eq. wt 1}}{\text{eq. wt 2}}$$

$$\text{eq. wt} = \frac{\text{molar mass}}{\text{valency}}$$

$$\text{Cu}^{2+} \text{ eq. wt} = \frac{63}{2} = 31.5 \text{ gm}$$

$$\text{Ag}^+ \text{ eq. wt} = \frac{108}{1} = 108 \text{ gm}$$

$$\frac{3.175 \text{ gm}}{w} = \frac{31.75}{108}$$

$$w_2 = \frac{3.175 \times 108}{31.75} = 10.8 \text{ gm}$$

$\therefore$  The weight of silver deposited is 10.8 grams

Que-5 4.5 gm of Al deposited at cathode from Al<sup>3+</sup> sol<sup>n</sup> by a certain

quantity of electric charge, the volume of H<sub>2</sub> gas produced at STP from H<sup>+</sup> ion from the solution by the ~~same~~ passing eq. same quantity of electric charge

- (i) 44.8 L
- (ii) 22.4 L
- (iii) 5.6 L
- (iv) 11.2 L

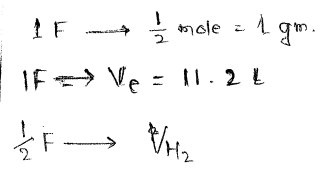


$$3F \rightarrow 27 \text{ gram}$$

$$\therefore 1F = 9 \text{ gram Al deposited.}$$

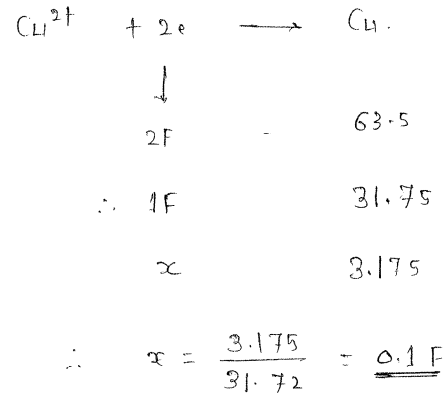
$$x = 4.5 \text{ gm}$$

$\therefore$  half F required to deposit 4.5 gm Al at cathode

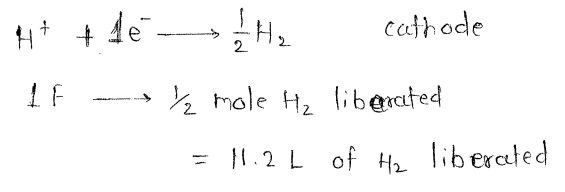


$$\therefore V_{H_2} = 5.6 \text{ L}$$

**Que-6** When a quantity of electricity is passed through  $\text{CuSO}_4$ , 3.175 gm of Cu get deposited, the same quantity of electricity is passed through  $\text{H}^+$  the volume of  $\text{H}_2$  liberated at STP is



0.1 F current is required to deposit Cu.



$$\therefore 0.1 F = \gamma$$

$$\therefore \gamma = 11.2 \times 0.1 = 1.12 F$$

$$= 1.12 \times 96,500 \text{ C}$$

**Que-7** S.R.P values of three metal cations A, B, C are 0.53 V, -3.25 V & -1.23 V respectively. The order of reducing power of the corresponding metal is

(i)  $C > B > A$       (ii)  $A > B > C$       (iii)  $A > C > B$       (iv)  $B > C > A$ .

strong reducing agent  $\propto$  low reduction potential.

$$\left. \begin{array}{l} \text{reducing character} \propto \frac{1}{\text{reduction potential.}} \\ \text{reducing character} \propto \text{oxid}^n \text{ potential.} \end{array} \right\}$$

$$\therefore \text{S.R.P increasing order} : B (-3.25 \text{ V}) < C (-1.23 \text{ V}) < A (0.53 \text{ V})$$

$\therefore$  order of reducing power  $: B > C > A$ .  $\therefore$  option (iv) is the correct answer

**Que-8** Specific conductance of 500 ml solution containing 4.9 gm of  $\text{H}_2\text{SO}_4$  is 0.025  $\text{cm}^{-1}$  calculate  $\lambda_c$  &  $\mu_c$ .

$$\rightarrow V = 500 \text{ ml.}$$

$$W = 4.9 \text{ gm}$$

$$K = 0.02 \text{ } \Omega^{-1} \text{ cm}^{-1}$$

$$\text{conc.} = \frac{W}{M \times V} \times \frac{1000}{500} = \frac{4.9}{98.20} \times 2 = \frac{1}{10} = 0.1 \text{ M.}$$

$$\mu_c = \frac{1000 K}{C_m} = \frac{1000 \times 0.02}{0.1} = \frac{1000 \times 0.2}{1}$$

$$= 200 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\lambda = \frac{-4}{2} = \frac{200}{2} = 100 \text{ } \Omega^{-1} \text{ cm}^{-1} \text{ gm. eq}^{-1}$$

Que-9 Eq. conductance at  $\infty$  dilution of acetic acid is  $300 \text{ } \Omega^{-1} \text{ cm}^{-1} \text{ gm. eq}^{-1}$ .

$$K = 3 \times 10^{-4} \text{ } \Omega^{-1} \text{ cm}^{-1} \quad \& \quad C_N = 0.01 \text{ N} \quad \text{Calculate } \alpha = ?$$

$$\Rightarrow \lambda_{\infty} = 300 \text{ } \Omega^{-1} \text{ cm}^{-1} \text{ gm. eq}^{-1} \quad \left| \quad \lambda_c = \frac{1000 K}{C_N} = \frac{1000 \times 3 \times 10^{-4}}{10^{-2}} \right| \quad \left| \quad \alpha = \frac{\lambda_c}{\lambda_{\infty}} = \frac{30}{300} = \frac{1}{10} \right.$$

$$K = 3 \times 10^{-4} \text{ } \Omega^{-1} \text{ cm}^{-1} \quad \left| \quad \lambda_c = 3 \times 10^{-1} \times 10^2 \right| \quad \left| \quad \boxed{\alpha = 0.1} \text{ or } 10\% \right.$$

$$C_N = 0.01 \text{ N} = 10^{-2} \text{ N.} \quad \left| \quad \lambda_c = 30 \right| \quad \left| \quad \text{degree of ionization is } 0.1 \right.$$

$$\alpha = ?$$

Que-10  $\alpha$  is maximum (cell constant) in case of

(i) wire of length 100 cm &  $a = 100 \text{ cm}^2$

(ii)  $l = 10 \text{ cm}$  &  $a = 10 \text{ cm}^2$

(iii)  $1 \text{ cm}^3$  of a material.

(iv) equal in all cases

$$\Rightarrow \text{cell constant, } \alpha = \frac{l}{a} \quad \text{(iii) } \alpha = \frac{l}{1} = 1 \text{ cm}^{-1}$$

(i)  $\alpha = \frac{100}{100} = 1 \text{ cm}^{-1}$   $\therefore$  option (iv) is the correct answer.

$$(ii) \alpha = \frac{10}{10} = 1 \text{ cm}^{-1}$$

Que-11 The specific conductance of a soln is  $0.176 \text{ } \Omega^{-1} \text{ cm}^{-1}$ . The cell constant is  $0.255 \text{ cm}^{-1}$ . The conductance in  $\Omega^{-1}$  of that soln is.

- (i) 1.449      (ii) 0.690      (iii) 0.045      (iv) 0.431

$$\rightarrow K = 0.176 \text{ } \Omega^{-1} \text{ cm}^{-1}$$

$$\alpha = 0.255 \text{ cm}^{-1}$$

$$\boxed{K = \alpha \cdot C}$$

$$C = ?$$

$$\boxed{C = \frac{K}{\alpha}}$$

$$C = \frac{0.176}{0.255} = \frac{176}{255} = 0.690 \text{ } \Omega^{-1}$$

$\therefore$  option (ii) is the correct answer.

Que-12 The specific conductance of an electrolyte soln is  $0.2 \text{ } \Omega^{-1} \text{ cm}^{-1}$  and cell constant is  $0.25 \text{ cm}^{-1}$ . The conductance of solution is

- (i)  $1.25 \text{ } \Omega^{-1}$       (ii)  $1.0 \text{ } \Omega^{-1}$       (iii)  $0.8 \text{ } \Omega^{-1}$       (iv)  $2.0 \text{ } \Omega^{-1}$

$$\rightarrow K = 0.2 \text{ } \Omega^{-1} \text{ cm}^{-1}$$

$$\alpha = 0.25 \text{ cm}^{-1}$$

$$C = \frac{K}{\alpha} = \frac{0.20}{0.25} = \frac{20}{25} = \frac{4}{5} = 0.8 \text{ } \Omega^{-1}$$

$$C = ?$$

$$C = 0.8 \text{ } \Omega^{-1}$$

$\therefore$  option (iii) is the correct answer.

(i) potential developed on M when it is in contact with soln  $M^{n+}$  of any conc.

(ii) The energy required to deposit 1 eq. of M on electrode M.

(iii) The current required to deposit 1 eq. of metal on electrode M.

(iv) The potential developed on M, when it is in contact with soln of  $M^{n+}$  of unit molar conc.

→ condition: 25°C. - temp  
: 1M - conc.

∴ option (iv) is the correct answer.

## # Nernst Equation. (Hotstar/Hotspot of CSIR-NET) ☆☆☆☆☆

⇒ relation between electrode potential & conc. of electrolyte. (because temp. is taken as fixed)

⇒ from thermodynamic,

$$\boxed{\Delta G = \Delta G^\circ + RT \ln K} \quad K: \text{reaction quotient} = Q_c$$

At eq<sup>m</sup>  $\Delta G = 0$ .

$$0 = \Delta G^\circ + RT \ln K$$

$$\therefore \boxed{\Delta G^\circ = -RT \ln K}$$

we know that

$$\Delta G = -nFE$$

$$\boxed{\Delta G^\circ = -nFE^\circ}$$

at any condition

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^\circ + RT \ln Q_c$$

$$\boxed{E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q_c}$$

$$K = \text{Reaction Quotient} = Q_c$$

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q_c$$

$$\boxed{E = E^\circ - \frac{0.059}{n} \log Q_c}$$

—  $Q_c$  : Reaction Quotient.

$$E = E^\circ - \frac{RT}{nF} \ln K = E^\circ - \frac{2.303 RT}{nF} \log K = E^\circ - \frac{0.059}{n} \log K$$

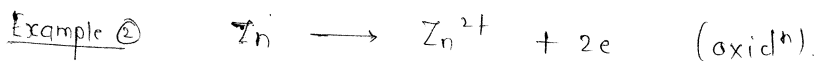


$$E_{Cu/Cu^{2+}} = E^\circ_{Cu/Cu^{2+}} - \frac{0.059}{2} \log \frac{a_{Cu^{2+}}}{a_{Cu}}$$

$a_{Cu^{2+}}$  - activity of  $Cu^{2+}$   
 $a_{Cu}$  - activity of  $Cu$

$$= E^\circ_{Cu/Cu^{2+}} - \frac{0.059}{2} \log [Cu^{2+}]$$

(∵ activity  $a = \gamma \cdot \text{conc}$   
for ideal sol<sup>n</sup>,  $\gamma = 1$ )



$$E_{Zn/Zn^{2+}} = E^\circ_{Zn/Zn^{2+}} - \frac{0.059}{2} \log \left( \frac{a_{Zn^{2+}}}{a_{Zn}} \right)$$

→  $\Delta G = -nFE_{cell}$

at equilibrium  $\Delta G = 0$   $E_{cell} = 0$

→ at equilibrium.

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln K$$

now  $K = \text{equilibrium constant}$

$$0 = E^\circ_{cell} - \frac{RT}{nF} \ln K$$

$$E^\circ_{cell} = \frac{RT}{nF} \ln K$$

$$\ln K = \frac{nFE^\circ}{RT}$$

$$\log K = \frac{nFE^\circ}{2.303 RT}$$

$$\log K = \frac{nE^\circ}{0.059}$$

$$\Delta G = -nFE_{cell}$$

(i) If  $E_{cell} = -ve$ , then  $\Delta G = +ve$   
 $\Rightarrow$  non-spontaneous cell reaction

(ii) If  $E_{cell} = +ve$ , then  $\Delta G = -ve$   
 $\Rightarrow$  spontaneous cell reaction occurs

→ calculation of thermodynamic quantities

$$(i) \quad \Delta G^\circ = -nFE_{cell}^\circ \quad \& \quad \Delta G = nFE_{cell}$$

$$(ii) \quad \left[ \frac{\partial(\Delta G)}{\partial T} \right]_p = -\Delta S$$

$$\Rightarrow -\Delta S = \left[ \frac{\partial}{\partial T} (-nFE_{cell}) \right]$$

$$(iii) \quad nF \left( \frac{\partial E_{cell}}{\partial T} \right)_p = \Delta S$$

$$\left( \frac{\partial E_{cell}}{\partial T} \right)_p = \frac{\Delta S}{nF}$$

$$\left( \frac{\partial E_{cell}}{\partial T} \right)_p \equiv \text{temp. coefficient}$$

$$(iii) \quad \Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta G + T\Delta S$$

$$= -nFE_{cell} + T \cdot nF \left( \frac{\partial E_{cell}}{\partial T} \right)_p$$

$$\Delta H = nF \left\{ T \left( \frac{\partial E_{cell}}{\partial T} \right)_p - E_{cell} \right\}$$

$$\Rightarrow \frac{\partial E_{cell}}{\partial T} = \frac{\Delta H}{nFT} + \frac{E_{cell}}{T}$$

(1 volt. Coulomb = 1 J)

→ standard electrode potential calculation of reaction.



$$\Delta G_3^\circ = \Delta G_1^\circ + \Delta G_2^\circ$$

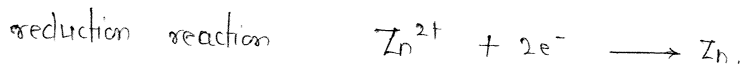
$$-n_3 FE_3^\circ = -n_1 FE_1^\circ - n_2 FE_2^\circ$$

$$n_3 E_3^\circ = n_1 E_1^\circ + n_2 E_2^\circ$$

$$E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3}$$

Que-1 The standard red<sup>n</sup> potential of Zn is  $-0.76$  V. Calculate reduction potential of  $0.01$  M  $ZnSO_4$  solution at  $25^\circ C$

$$\rightarrow E_{cell}^{\circ} = -0.76 \text{ V}, \quad [Zn^{2+}] = 0.01 \text{ M} = 10^{-2} \text{ M.}$$



$$E_{Zn^{2+}/Zn} = E_{Zn^{2+}/Zn}^{\circ} - \frac{RT}{nF} \ln \frac{1}{[Zn^{2+}]} \quad \therefore \boxed{E_{Zn^{2+}/Zn} = -0.819 \text{ V}}$$

$$= -0.76 - \frac{0.059}{2} \log \frac{1}{10^{-2}}$$

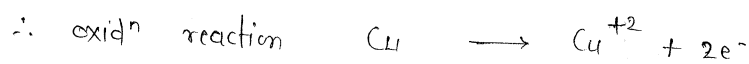
$$= -0.76 - \frac{0.059}{2} \log 10^2$$

$$= -0.76 - \cancel{2} \times \frac{0.059}{\cancel{2}} \log 10$$

$$= -0.760 - 0.059$$

Que-2 The standard red<sup>n</sup> potential of Cu is  $+0.34$  V. Calculate oxid<sup>n</sup> potential of  $0.01$  M  $CuSO_4$  solution at  $25^\circ C$ .

$\rightarrow$  We have to calculate oxidation potential



$$E_{Cu/Cu^{2+}} = E_{Cu/Cu^{2+}}^{\circ} - \frac{0.059}{2} \log [Cu^{2+}]$$

red<sup>n</sup> potential =  $+0.34$  V

$\therefore$  oxid<sup>n</sup> potential =  $-0.34$  V

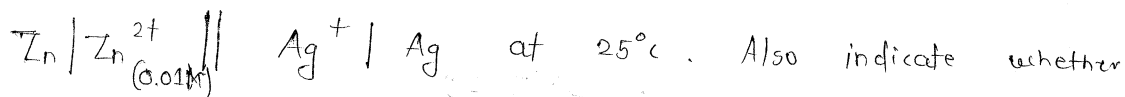
$$= -0.34 - \frac{0.059}{2} \log 10^{-2}$$

$$= -0.34 - \frac{0.059}{2} \times (-2)$$

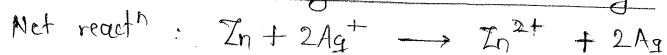
$$= -0.34 + 0.059$$

$$= -0.28 \text{ V.}$$

Que-3 Standard red<sup>n</sup> potential of Zn & Ag electrode are  $-0.76$  V &  $+0.80$  V respectively. Calculate the potential of



the cell reaction is spontaneous or not.



$$E_{\text{cell}} = E_{\text{cell}} - \frac{0.059}{2} \log \frac{1}{[\text{Ag}^+]^2}$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}} - E_{\text{anode}} \quad (\text{red}^n \text{ potential}) \\ &= 0.80 - (-0.76) \\ &= 1.56 \text{ V} \end{aligned}$$

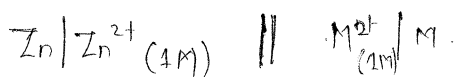
$$\begin{aligned} \therefore E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{10^{-2}}{10^{-2}} \\ &= 1.56 - \frac{0.059}{2} \log 1 \quad \because \log 1 = 0 \end{aligned}$$

$$\boxed{E_{\text{cell}} = 1.56}$$

$E_{\text{cell}} = +ve \rightarrow \Delta G = -ve \Rightarrow$  spontaneous reaction.

Que-4 What is the cell emf in volts of the following cell at 25°C

$$E_{\text{cell}}^{\circ} = 1.53 \text{ V.}$$

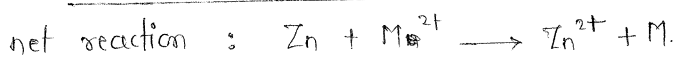
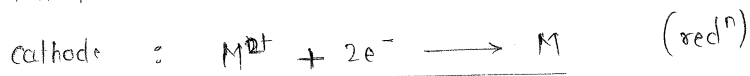


(i) 1.53

(ii) 1.471

(iii) 1.589

(iv) 1.402



$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left( \frac{RT}{nF} \right) \log \frac{[\text{Zn}^{2+}]}{[\text{M}^{2+}]}$$

$$\therefore \boxed{E_{\text{cell}} = 1.53 \text{ V}}$$

$$= 1.53 - \frac{0.059}{2} \log 1$$

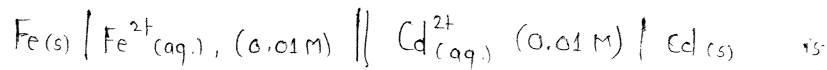
$$= 1.53 - 0 \quad (\because \log 1 = 0)$$

Que-5 The electrochemical cell potential after reactants & products react at equilibrium is

→  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln K$  at equilibrium  $E_{\text{cell}} = 0$

$$\therefore E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K = \frac{2.303 RT}{nF} \log K = \frac{0.059}{n} \log K$$

Que-6 The predicted e.m.f of electrochemical cell



$$E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.447 \text{ V.}$$

$$E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} = -0.403 \text{ V.}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Cd}^{2+}/\text{Cd}}^{\circ} (\text{cathode}) - E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} (\text{anode}) \quad \text{--- red}^{\circ} \text{ potential}$$

$$= -0.403 - (-0.447)$$

$$= -0.403 + 0.447$$

$$E_{\text{cell}}^{\circ} = +0.044 \text{ V}$$

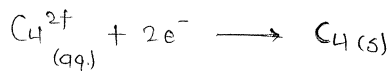
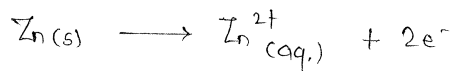
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Fe}^{2+}]}{[\text{Cd}^{2+}]}$$

$$= E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log 1$$

$$E_{\text{cell}} = 0.044 \text{ V}$$

$$\because \log 1 = 0$$

Que-7 The correct  $\Delta G$  for the cell react<sup>n</sup> involving steps



$$(i) \Delta G^{\circ} - RT \ln \left( \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$$

$$(ii) \Delta G^{\circ} + RT \ln \left( \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$$

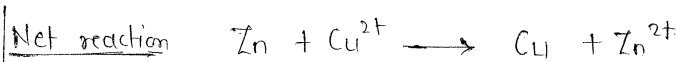
$$(iii) \Delta G^{\circ} + \frac{RT}{nF} \ln \left( \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$$

$$(iv) \Delta G^{\circ} - \frac{RT}{nF} \ln \left( \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$$

→ A/c Nernst Equation.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln K$$

$$\Rightarrow \Delta G = \Delta G^{\circ} + RT \ln K$$

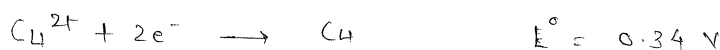
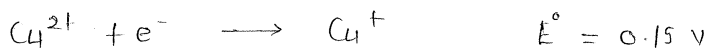


$$\Delta G = \Delta G^{\circ} + RT \ln \left( \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$$

$\therefore$  option (ii) is the correct answer

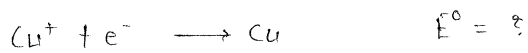
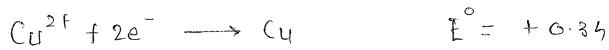
Que-8

The half cell reaction are.



Calculate  $E^{\circ}$  of half cell react<sup>n</sup>  $\text{Cu}^{+} + e^{-} \longrightarrow \text{Cu}$





$$E_3^\circ = \frac{n_1 E_1^\circ + E_2^\circ n_2}{n_3} = \frac{1 \times -0.15 + 2 \times (+0.34)}{1} = -0.15 + 0.68 = +0.53$$

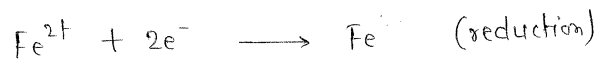
$$\boxed{E_3^\circ = +0.53 \text{ V}}$$

Que-9 Standard Electrode potential of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Fe}^{2+}/\text{Fe}$  are  $+0.77 \text{ V}$ ,  $-0.44 \text{ V}$  resp. at  $300 \text{ K}$ . The  $E^\circ$  of  $\text{Fe}^{3+}/\text{Fe}$  electrode at the same temp. is.

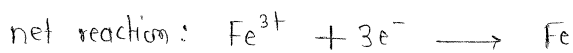
- (i)  $1.21 \text{ V}$       (ii)  $0.33 \text{ V}$       (iii)  $-0.11 \text{ V}$       (iv)  $-0.04 \text{ V}$



$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = +0.77 \text{ V}$$



$$E_{\text{Fe}^{2+}/\text{Fe}}^\circ = -0.44 \text{ V}$$



$$E_{\text{Fe}^{3+}/\text{Fe}}^\circ = ?$$

$$3 E_{\text{Fe}^{3+}/\text{Fe}}^\circ = 1 E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ + 2 E_{\text{Fe}^{2+}/\text{Fe}}^\circ$$

$$E_{\text{Fe}^{3+}/\text{Fe}}^\circ = \frac{0.77 - 0.44 \times 2}{3} = \frac{0.11}{3} = -0.04 \text{ V}$$

OR

$$E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3} = \frac{1 \times 0.77 + 2 \times (-0.44)}{3} = \frac{0.77 - 0.88}{3} = \frac{-0.11}{3}$$

$$\therefore \boxed{E_3^\circ = -0.04 \text{ V}}$$

Que-10

$$E_{\text{M}^{3+}/\text{M}^{2+}}^\circ = 1.51 \text{ V}$$

$$E_{\text{M}^{4+}/\text{M}^{2+}}^\circ = 1.23 \text{ V} \quad \Rightarrow \quad E_{\text{M}^{2+}/\text{M}^{4+}}^\circ = -1.23 \text{ V}$$

$$E_{\text{M}^{3+}/\text{M}^{4+}}^\circ = 1.51 \text{ V}$$

$$E_{\text{M}^{2+}/\text{M}^{4+}}^\circ = -1.23 \text{ V}$$

$$E_{\text{M}^{3+}/\text{M}^{4+}}^\circ = ?$$

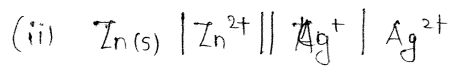
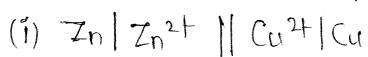
$$E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3} = \frac{1.51 + 2(-1.23)}{3}$$

$$= \frac{1.51 - 2.46}{3}$$

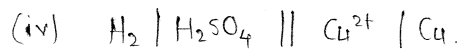
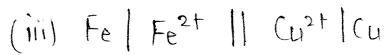
$$= \frac{-1.05}{3}$$

$$\boxed{E_3^\circ = -0.35}$$

Que-9 Daniel cell is represented by



⇒ option (i) is the correct answer



Que-10  $K_{eq} = ?$  for  $2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}$  is

given that

$$\left\{ \begin{array}{l} E^\circ_{Fe^{3+}/Fe^{2+}} = 0.75 V \\ E^\circ_{Sn^{4+}/Sn^{2+}} = 0.15 V \\ \frac{2.303 RT}{F} = 0.06 \end{array} \right. \quad \begin{array}{l} \text{(i) } 10^{10} \\ \text{(ii) } 10^{20} \\ \text{(iii) } 10^{30} \\ \text{(iv) } 10^{40} \end{array}$$

$$\log K = \frac{n \cdot E^\circ_{cell}}{0.06} \quad n = 2$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} \quad \text{--- red}^n \text{ potential}$$

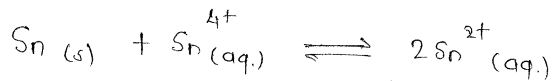
$$= 0.75 - 0.15$$

$$= 0.60$$

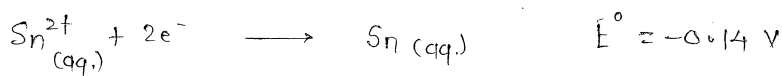
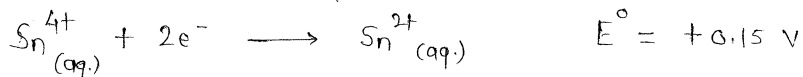
$$\log K = \frac{2 \times 0.6}{0.06} = 20$$

$$\boxed{K = 10^{20}}$$

Que-11 For the cell reaction.



The separate electrode reaction to be with respect to <sup>std</sup> electrode potential at 25°C.



$$\frac{RT}{F} = 25.7 \text{ mV} \quad \ln K = ?$$

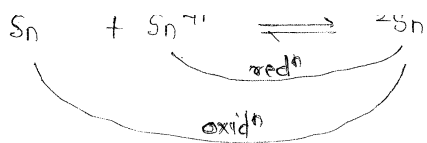
(i) 22.6

(ii) 226

(iii) 2.26

(iv)  $2.26 \times 10^{-1}$

$$\rightarrow \ln K = \frac{n \cdot E^\circ_{cell} \cdot F}{RT} = \frac{n \cdot E^\circ_{cell}}{25.7 \text{ mV}}$$



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \quad \text{--- red}^n \text{ potential}$$

$$= 0.15 \text{ V} - (-0.14 \text{ V})$$

$$= 0.29 \text{ V}$$

$$\ln K = \frac{2 \times 0.29}{25.7 \times 10^{-3}} = \frac{2 \times 290}{25.7} \approx \underline{\underline{22.6}}$$

Que-12 Which ~~one~~ is correct for redox reaction.



(i)  $E = E^{\circ} - RT \ln \frac{[\text{O}]}{[\text{R}]}$

(ii)  $\frac{[\text{O}]}{[\text{R}]} = e^{\frac{nF}{RT}(E-E^{\circ})}$

(iii)  $\frac{[\text{O}]}{[\text{R}]} = e^{-\frac{nF}{RT}(E-E^{\circ})}$

(iv)  $\frac{[\text{O}]}{[\text{R}]} = e^{\frac{nF}{RT}(E+E^{\circ})}$

→

$$E = E^{\circ} - \frac{RT}{nF} \log \frac{[\text{R}]}{[\text{O}]}$$



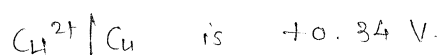
$$\frac{RT}{nF} \ln \frac{[\text{R}]}{[\text{O}]} = E^{\circ} - E$$

$$\ln \frac{[\text{R}]}{[\text{O}]} = \frac{nF}{RT} (E^{\circ} - E)$$

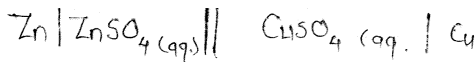
$$\ln \frac{[\text{O}]}{[\text{R}]} = \frac{nF}{RT} (E - E^{\circ})$$

$$\boxed{\frac{[\text{O}]}{[\text{R}]} = e^{\frac{nF}{RT} (E - E^{\circ})}}$$

Que-13 The cell voltage of Daniel Cell is 1.07 V. If red<sup>n</sup> potential of



Daniel cell



(i) 1.41 V

(ii) -1.41 V

(iii) 0.73 V

(iv) -0.73 V

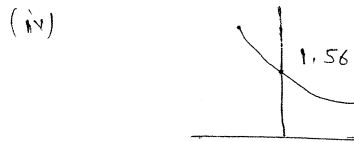
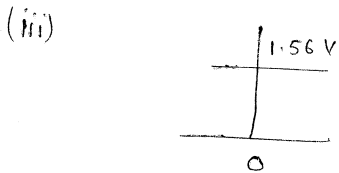
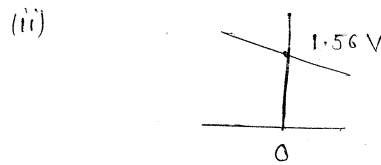
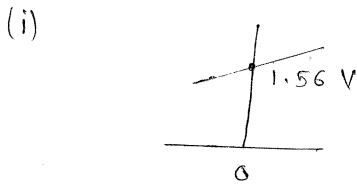
→  
 Que-14 Which graph correctly correlates  $E_{\text{cell}}$  as function of conc. for the cell



$$E^{\circ}_{\text{cell}} = 1.56 \text{ V}$$

Y-axis:  $E_{\text{cell}}$

X-axis:  $\log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$



→

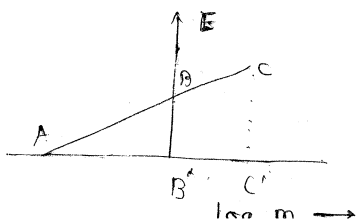
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.06}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$Y = c - mx$  — straight line

slope = -ve

∴ option (ii) is correct answer.

Que-15 The correct value of  $E^{\circ}$  for the reduction reaction, the following graph of  $E$  v/s  $\log m$  ( $m = \text{molarity}$ )



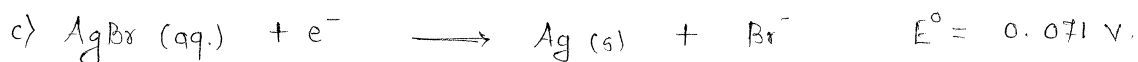
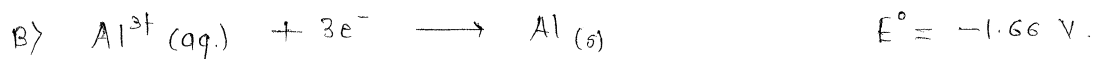
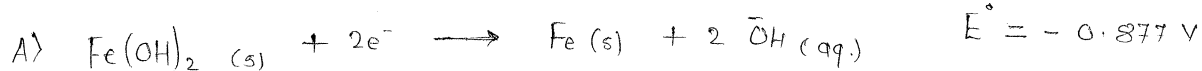
$$y = \frac{c}{m} - \frac{mx}{n} \quad \text{--- straight line}$$

$\downarrow$  intercept       $\downarrow$  slope

intercept :  $BB'$  —  $E^\circ$  value

slope :  $BC$  —  $\frac{0.06}{n}$

Que-16



The overall reaction for the cell, the direction of spontaneous change would be.

cell with A & B

cell with A & C.

(i) Fe reduced

Fe reduced

(ii) Fe reduced

Fe oxidized

(iii) Fe oxidized

Fe oxidized

(iv) Fe oxidized

Fe reduced

→

Que-17

The std cell potential for the reaction.



is 1.10 V. The  $\Delta G$  for the reaction is

(i)  $-21.2 \text{ kJ. mol}^{-1}$

(ii)  $21.2 \text{ kJ. mol}^{-1}$

(iii)  $212 \text{ kJ.mol}^{-1}$

(iv)  $-212 \text{ J.mol}^{-1}$

$\rightarrow \Delta G = -nFE_{\text{cell}}$

$= -2 \times 96,500 \times 1.1 \text{ J}$

$= -2 \times 96.5 \times 1.1 \text{ kJ}$

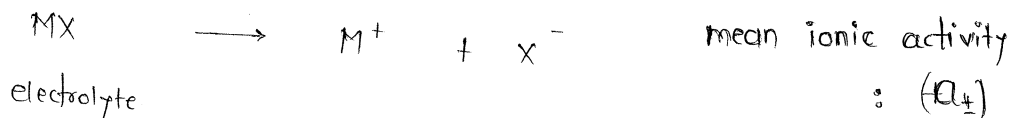
=

# mean ionic activity ( $a_{\pm}$ ) & mean ionic activity coefficient ( $\gamma_{\pm}$ ) - measures the deviation from ideal behaviour.

$\rightarrow$  Non-electrolytic solution : ion-ion interaction absent.  
: No deviation from ideal behaviour.

$\Rightarrow$  electrolytic solution : ion-ion interactions are present  
(NaCl, KCl) : we get deviation from ideal behaviour.

Example



conc.  $m$   $m$   $m$  mean ionic activity coefficient :  $(\gamma_{\pm})$   
activity :  $a$

$a = \gamma \cdot \text{conc}$

$a$  - activity  
 $\gamma$  - activity coefficient  
conc. -  $m$  - molality.

$a = \gamma \cdot m$

for cation  $a_+ = \gamma_+ \cdot m$

for anion  $a_- = \gamma_- \cdot m$

$\left\{ \begin{matrix} a_+, a_- \\ \gamma_+, \gamma_- \end{matrix} \right\}$  cannot obtain experimentally

Activity of electrolyte  $a = a_+ \cdot a_-$

$a = (a_{\pm})^2$

$x, y$  mean =  $(xy)^{1/2} = \sqrt{xy}$

$x, y, z$  mean =  $(x \cdot y \cdot z)^{1/3}$

$x, x, y, z$  mean =  $(x^2 \cdot y \cdot z)^{1/4}$

similarly

$a_+, a_-$

mean =  $(a_+ \cdot a_-)^{1/2} = (a_{\pm})^2$

or

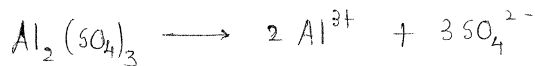
$a = \gamma_+ \cdot m \cdot \gamma_- \cdot m$

$a = (\gamma_+ \cdot \gamma_-) \cdot m^2$

$a = (\gamma_{\pm} \cdot m)^2$



$$\left\{ \begin{array}{l} \dots \\ \Rightarrow \gamma_+ \cdot \gamma_- = (\gamma_{\pm})^2 \end{array} \right.$$



$$m \qquad \qquad 2m \qquad \qquad 3m$$

$$m \qquad \qquad xm \qquad \qquad \gamma m$$

$$a_+ = \gamma_+ \cdot xm$$

$$a_- = \gamma_- \cdot \gamma m$$

$$a = a_+^x \cdot a_-^y$$

$$\left\{ \begin{array}{l} \text{means } (a_{\pm}) = (a_+^x \cdot a_-^y)^{\frac{1}{x+y}} \\ \Rightarrow (a_{\pm})^{x+y} = a_+^x \cdot a_-^y \end{array} \right.$$

$$\therefore a = a_+^x \cdot a_-^y$$

$$\boxed{a = (a_{\pm})^{x+y}}$$

Important formulae

$$\rightarrow (a_{\pm})^{x+y} = a_+^x \cdot a_-^y$$

$$(a_{\pm}) = \text{mean ionic activity}$$

$$\rightarrow (\gamma_{\pm})^{x+y} = \gamma_+^x \cdot \gamma_-^y$$

$$(\gamma_{\pm}) = \text{mean ionic activity coefficient}$$

or

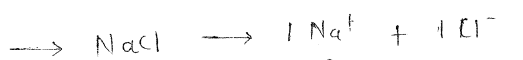
$$a = (\gamma_+ \cdot xm)^x (\gamma_- \cdot \gamma m)^y$$

$$= \gamma_+^x \cdot \gamma_-^y \cdot x^x \cdot \gamma^y \cdot m^x \cdot m^y$$

$$= (\gamma_+ \cdot \gamma_-)^{x+y} x^x \cdot \gamma^y (m)^{x+y}$$

$$\boxed{a = (\gamma_{\pm} \cdot m)^{x+y} x^x \cdot \gamma^y}$$

activity of electrolyte.



$$\text{mean } (a_{\pm})^2 = a_+^1 \cdot a_-^1$$

$$\text{mean } (\gamma_{\pm})^2 = \gamma_+^1 \cdot \gamma_-^1$$



$$x=2 \quad y=1$$

$$(a_{\pm})^{x+y} = a_+^x \cdot a_-^y$$

$$(a_{\pm})^3 = a_+^2 \cdot a_-^1$$

$$(\gamma_{\pm})^{x+y} = \gamma_+^x \cdot \gamma_-^y$$

$$(\gamma_{\pm})^3 = \gamma_+^2 \cdot \gamma_-^1$$

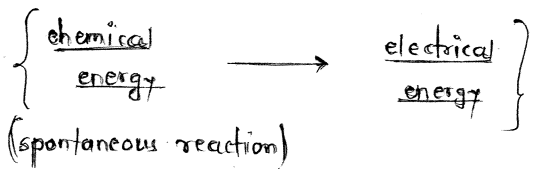


$$x=3, y=2$$

$$(a_{\pm})^5 = a_+^3 \cdot a_-^2$$

$$(\gamma_{\pm})^5 = \gamma_+^3 \cdot \gamma_-^2$$

# Galvanic cell



decrease in  $G$  is directly proportional to  $E_{\text{cell}}$

$$\Delta G = -ve$$

$$-\Delta G = nFE_{\text{cell}}$$

$$E_{\text{cell}} = +ve$$

The cell in which free energy of spontaneous reaction is converted to electrical energy is called galvanic cell.

⇒ classification

## Galvanic Cell

### chemical cell

→ emf produced is due to chemical reaction

### concentration cell

→ emf is produced due to transfer of matter from high conc → low conc.

#### Chemical cell without transference

→ No transfer of ions from one half cell to another.

Ex: Daniel Cell

#### chemical cell with transference

→ mixing of ions from two half cell containing electrolyte.

## conc. cell

### Electrode conc. cell

### Electrolyte conc. cell

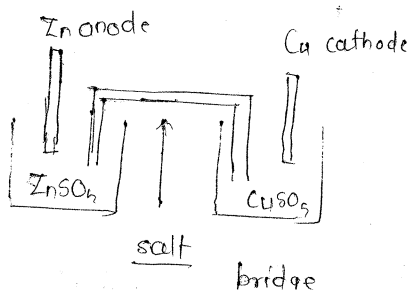
#### electrolyte conc. cell without transference

#### electrolyte conc. cell with transference

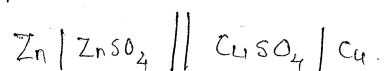
## 1) Chemical Cell without transference.

Ex: Daniel Cell.

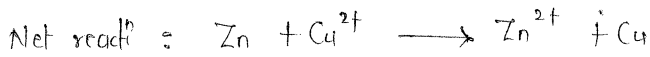
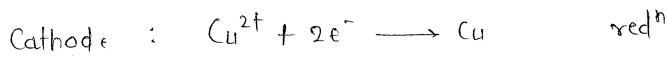
→ Here no transfer of ions from one half cell to another half cell takes place.



cell representation:





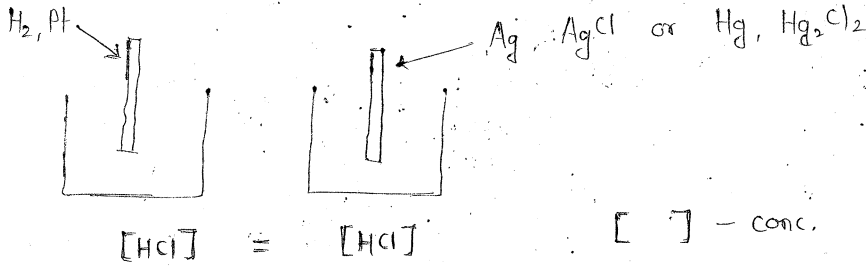


A/c Nernst equation.

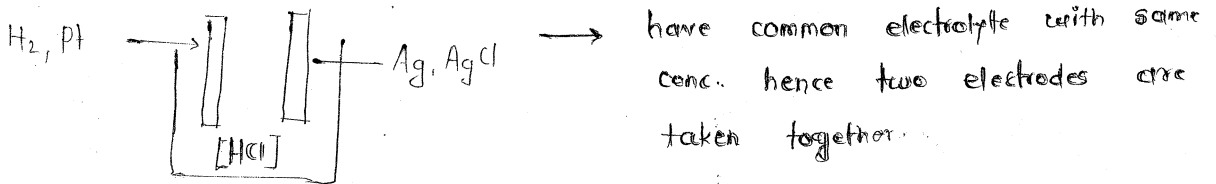
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$$

(n=2)

Example @

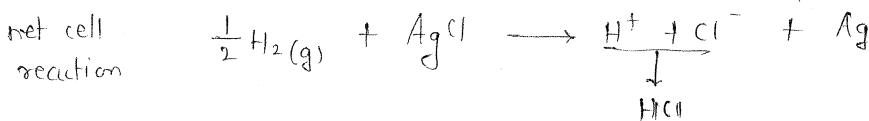
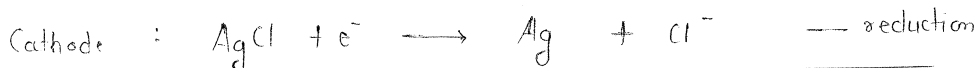
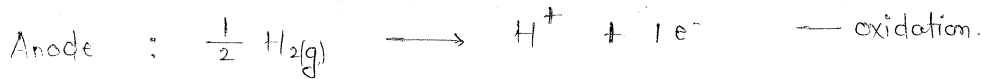
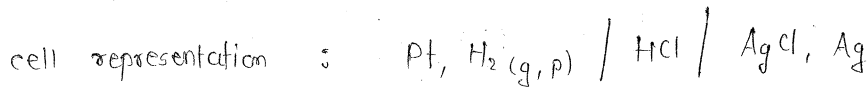


Pt is used for electrical contact



chemical cell without transference

because conc.  $[\text{HCl}]$  is same and no transfer occurs. ~~from~~ due to no. difference in concentration.



A/c Nernst equation :

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{1F} \ln \frac{a_{\text{HCl}}}{p^{1/2}}$$

pressure of gas liberated or used = conc. of it. = activity of it.

$E^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$  (red<sup>n</sup> potential)

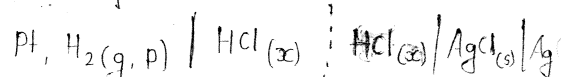
$$E_{\text{cell}} = E_{\text{AgCl}/\text{Ag}} - E_{\text{H}^+/\text{H}_2}$$

$$(\because E_{\text{H}^+/\text{H}_2}^{\circ} = 0)$$

$$E_{\text{cell}}^{\circ} = E_{\text{AgCl}/\text{Ag}}^{\circ} - 0$$

$$E_{\text{cell}}^{\circ} = E_{\text{AgCl}/\text{Ag}}^{\circ}$$

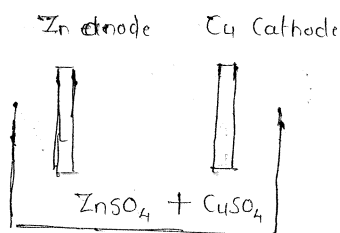
Cell representation :



$$E_{\text{cell}} = E_{\text{AgCl}/\text{Ag}}^{\circ} - \frac{RT}{F} \ln \frac{a_{\text{HCl}}}{p^{1/2}}$$

### (ii) Chemical cell with transference

Ex : Daniel Cell without salt bridge



- transfer of ions takes place from one half-cell to other, so some excess potential is observed which is called liquid junction potential ( $E_j$ )

(w.o.t) for without transference :  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$  (Red<sup>n</sup> potential) — (1)

(w.t) for with transference :  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} + E_j$  (red<sup>n</sup> pot.) — (2)

$$E_{\text{cell}} = E_{\text{w.o.t}} + E_j$$

$$E_{\text{w.t}} = E_{\text{w.o.t}} + E_j$$

$$E_j = E_{\text{w.t}} - E_{\text{w.o.t}}$$

→ Liquid Junction Potential can be calculated by using salt bridge.

salt bridge used :  $\text{NH}_4\text{NO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$

Used as salt bridge because

$$[t_+ = t_-] \quad t - \text{transport no.}$$

→ Salt bridge maintains the electrical neutrality in both the half cell.

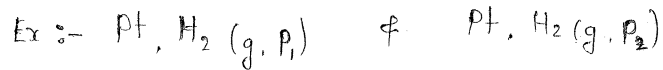
→ It also completes the circuit.

→ Agar-Agar / Gelatin gel - avoid mixing two electrolytes of two different half cell.

portance  
of  
salt  
bridge

→ there is difference in concentration of same electrode.

→ two same electrode but with different conc.



electrolyte    HCl

HCl

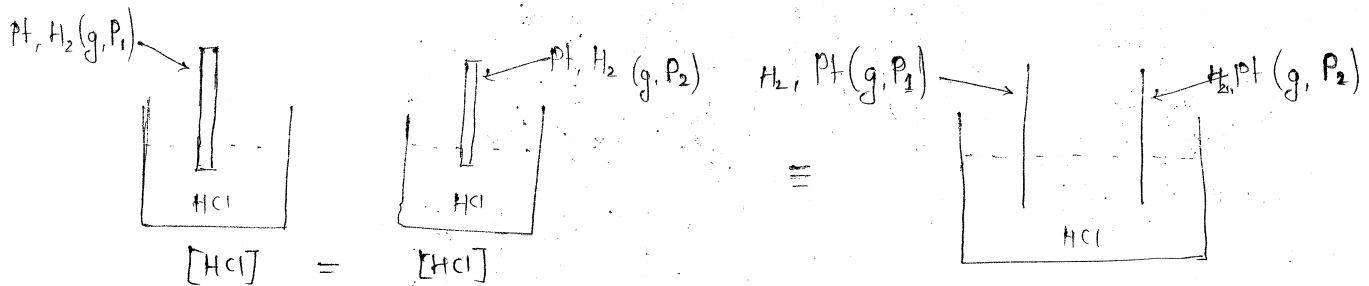
conc. of electrolyte

[HCl]

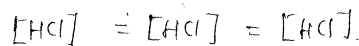
=

[HCl]

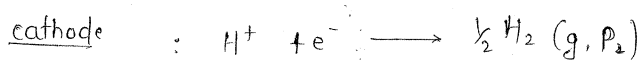
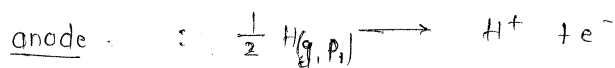
— same.



have same conc. of electrolyte.



cell representation : Pt, H<sub>2</sub> (g, P<sub>1</sub>) | HCl | Pt, H<sub>2</sub> (g, P<sub>2</sub>) — (This cell is reverse to or sensible to cation)



net cell reaction     $\frac{1}{2} \text{H}_2(\text{g}, P_1) \longrightarrow \frac{1}{2} \text{H}_2(\text{g}, P_2)$  — Here there is a physical change takes place. i.e. H<sub>2</sub> gas passes from P<sub>1</sub> to P<sub>2</sub>.

A/c Nernst Equation

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{1F} \ln \frac{P_2^{1/2}}{P_1^{1/2}}$$

$$E_{\text{cell}}^{\circ} = 0 = E_{\text{H}^+/\text{H}_2}^{\circ}$$

$$\therefore E_{\text{cell}} = - \frac{RT}{1F} \ln \left( \frac{P_2}{P_1} \right)^{1/2} = + \frac{RT}{1F} \ln \left( \frac{P_1}{P_2} \right)^{1/2}$$

$$E_{\text{cell}} = \frac{RT}{2F} \times \frac{1}{2} \ln \left( \frac{P_1}{P_2} \right) = \frac{RT}{2F} \ln \left( \frac{P_1}{P_2} \right)$$

$$E_{\text{cell}} = \frac{RT}{2F} \ln \left( \frac{P_1}{P_2} \right)$$

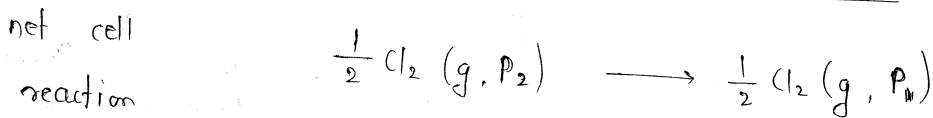
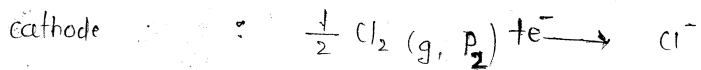
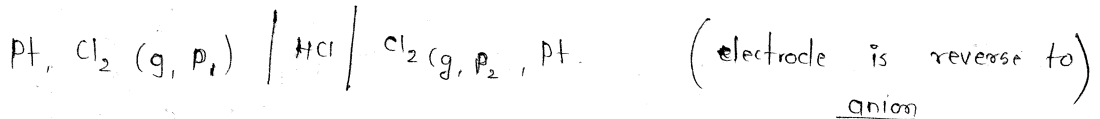
if  $P_1 > P_2 \Rightarrow E_{\text{cell}} = +ve \Rightarrow \Delta G = -ve \Rightarrow$  spontaneous.

$$E_{\text{cell}} = \frac{0.059}{2} \log \left( \frac{P_1}{P_2} \right)$$

$$E_{\text{cell}} = 0.03 \log \left( \frac{P_1}{P_2} \right)$$

$\leftarrow$   $H_2$  gas liberated from cathode only as  $P_1 \rightarrow P_2$  transfer takes place of  $H_2$  if  $P_1 > P_2$  & reaction is spontaneous

Example ②



A/c Nernst Equation.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{1F} \ln \left( \frac{P_1}{P_2} \right)^{1/2}$$

$\left\{ \begin{array}{l} \text{if anode \& cathode are} \\ \text{same} \\ \Rightarrow E_{\text{cell}}^{\circ} = 0 \end{array} \right\}$

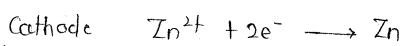
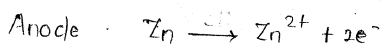
$$E_{\text{cell}} = - \frac{RT}{2F} \ln \left( \frac{P_1}{P_2} \right)$$

$$E_{\text{cell}} = + \frac{RT}{2F} \ln \left( \frac{P_2}{P_1} \right)$$

$H_2$  gas liberated at cathode only as  $Cl_2$  gas transfer from  $P_2 \rightarrow P_1$  and if  $P_2 > P_1$  and the reaction is spontaneous.

$$E_{\text{cell}} = \frac{0.06}{2} \log \frac{P_2}{P_1} = \boxed{0.03 \log \left( \frac{P_2}{P_1} \right) = E_{\text{cell}}}$$

Example ③ : cell representation :  $Hg - Zn(C_1) \mid ZnSO_4 \mid Zn - Hg(C_2)$



A/c Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0 \\ &= E_{Zn}^{\circ} - E_{Zn}^{\circ} = 0 \end{aligned}$$

$$\therefore E_{\text{cell}} = 0 - \frac{RT}{nF} \ln \left( \frac{C_2}{C_1} \right)$$

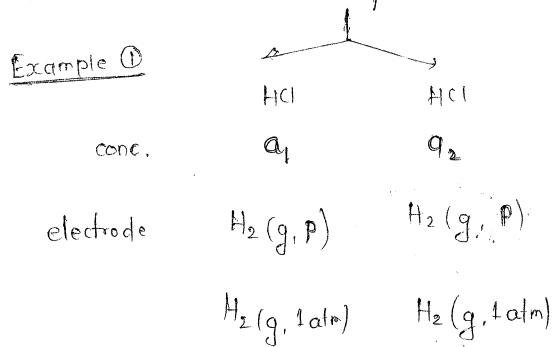
$$E_{\text{cell}} = + \frac{0.059}{2} \log \left( \frac{C_1}{C_2} \right) \quad \left( \because n=2 \text{ for abn cell} \right)$$

$$\boxed{E_{\text{cell}} = +0.03 \log \left( \frac{C_1}{C_2} \right)}$$

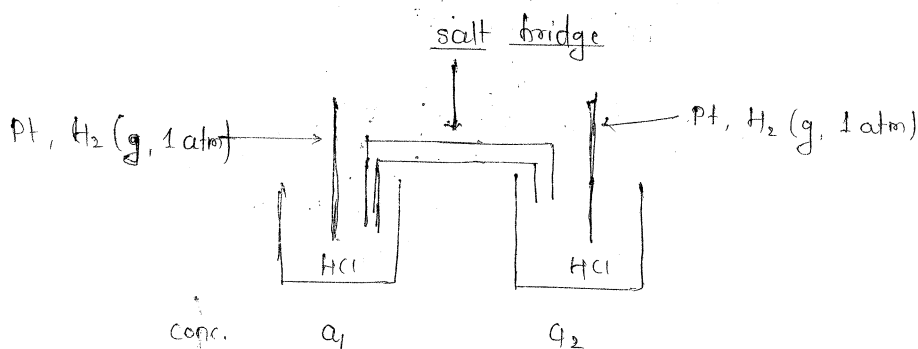
Zn transfer occurs from  $C_1 \rightarrow C_2$  conc. if  $C_1 > C_2$  & reaction is spontaneous.

(IV) Electrolyte conc. cell

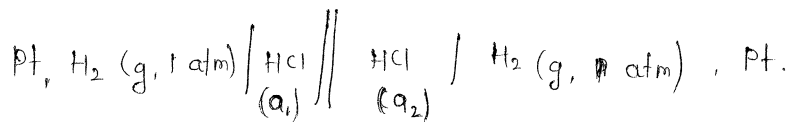
→ same electrolyte but with different conc.



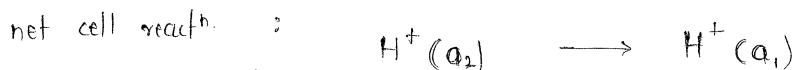
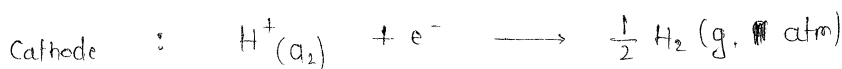
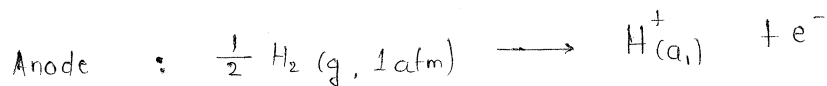
→ without transference of ion, we have to use salt bridge.



cell representation



(electrode reverse + cation)

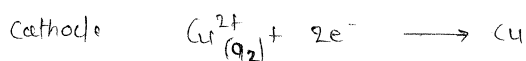


A/c Nernst equation :  $E_{\text{cell}} = - \frac{RT}{1 \cdot F} \ln \left( \frac{a_1}{a_2} \right) \quad \therefore E_{\text{cell}}^{\circ} = 0$

$$E_{\text{cell}} = \frac{RT}{1 \cdot F} \ln \left( \frac{a_2}{a_1} \right)$$

$$E_{\text{cell}} = 0.059 \log \left( \frac{a_2}{a_1} \right)$$

Example ②



net cell reaction



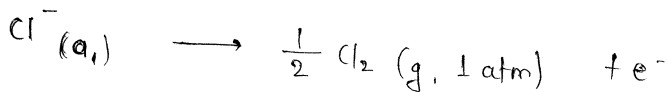
A/c Nernst equation : 
$$E_{\text{cell}} = \frac{RT}{2F} \ln \frac{a_2}{a_1} = \frac{0.059}{2} \log \left( \frac{a_2}{a_1} \right) = 0.03 \log \left( \frac{a_2}{a_1} \right)$$

Example 3

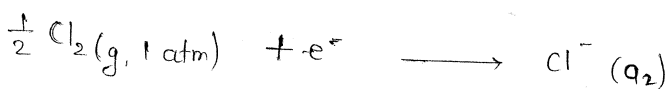


→ (electrode reverse to anion)

anode



cathode



net cell reaction



A/c Nernst equation.

$$E_{\text{cell}} = - \frac{RT}{1F} \ln \frac{a_2}{a_1} \quad \because E_{\text{cell}}^\circ = 0$$

$$E_{\text{cell}} = + \frac{RT}{1F} \ln \frac{a_1}{a_2} = 0.059 \times \log \left( \frac{a_1}{a_2} \right)$$

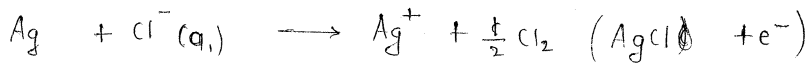
if  $a_1 > a_2 \implies E_{\text{cell}} = \text{+ve} \implies \Delta G = -\text{ve} \implies \text{spontaneous.}$

Example 4

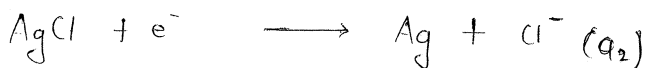


→ (Electrode reverse to anion)

anode



cathode



net cell reaction



A/c Nernst Equation

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right)$$

( $E_{\text{cell}}^\circ = 0$  because same electrode)

$$E_{\text{cell}} = - \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right)$$

if  $a_1 > a_2 \implies E_{\text{cell}} = \text{+ve}$

$\implies \Delta G = -\text{ve}$

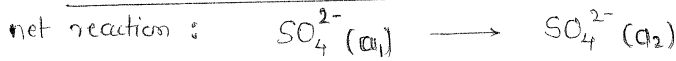
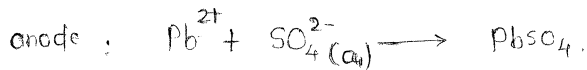
$\implies \text{spontaneous.}$

$$\therefore \boxed{E_{\text{cell}} = + \frac{RT}{nF} \ln \left( \frac{a_1}{a_2} \right)}$$

Example ②

Pb, PbSO<sub>4</sub> | SO<sub>4</sub><sup>2-</sup> (a<sub>1</sub>) || SO<sub>4</sub><sup>2-</sup> (a<sub>2</sub>) | Pt

(- to anion)



A/c Nernst Equation :  $E_{cell} = \frac{RT}{nF} \log \left( \frac{a_1}{a_2} \right)$

If  $a_1 > a_2 \implies E_{cell} = +ve$

$\implies \Delta G = -ve$

$\implies$  spontaneous reaction occurs

☆ Important formulae. ☆

Note

(i) Electrode reverse to cation.

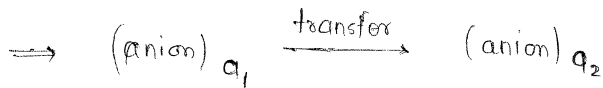


$\implies E_{cell} = \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right)$

a = activity / conc.

$\implies E_{cell} = \frac{RT}{nF} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1} \implies E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln \left( \frac{a_1}{a_2} \right)$

(ii) Electrode reverse to anion.



$\implies E_{cell} = \frac{RT}{nF} \ln \left( \frac{a_1}{a_2} \right)$

$\implies E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right)$

$\implies E_{cell} = \frac{RT}{nF} \ln \left( \frac{\gamma_1 \cdot m_1}{\gamma_2 \cdot m_2} \right)$

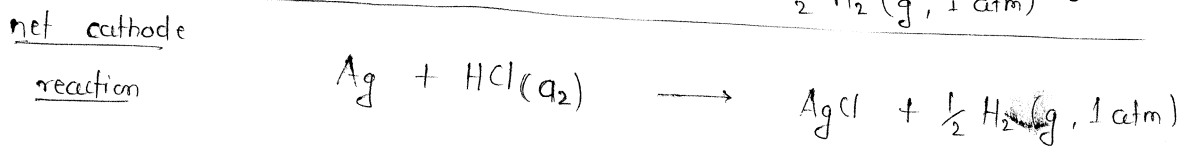
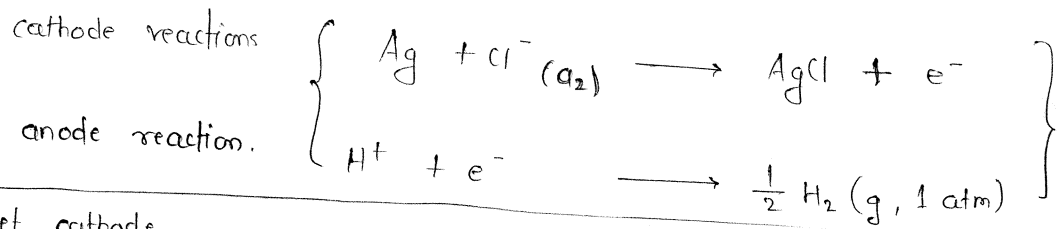
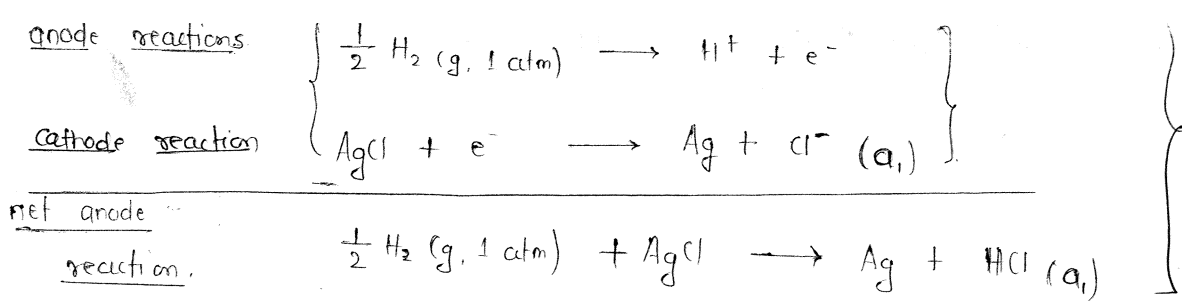
# By joining two chemical cell without transference in reverse direction

$\implies$  Electrolytic conc. cell without transference

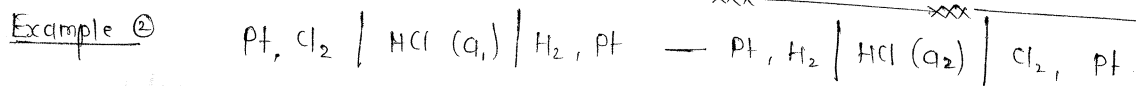
Example ①



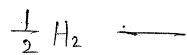
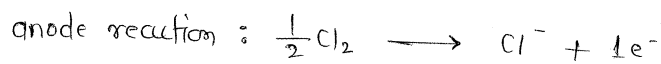
$\rightarrow$  End electrodes reverse to cation & middle electrode reverse to anion.



A/c Nernst eq<sup>n</sup> : 
$$E_{\text{cell}} = \frac{RT}{nF} \ln \frac{a_2}{a_1} = \frac{RT}{nF} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1}$$



→ End electrodes are reverse to ~~cation~~ anion and middle electrodes are reverse to cation.



$$E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{a_1}{a_2} \right) = 0.06 \log \left( \frac{a_1}{a_2} \right)$$



Note: (i) End electrodes reverse to anion



$$\Rightarrow E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right) = \frac{RT}{nF} \ln \left( \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1} \right) = \frac{RT}{nF} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

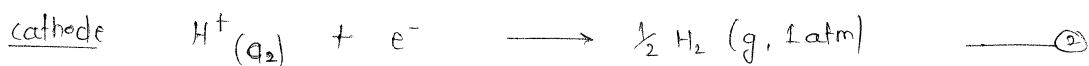
(ii) End electrodes reverse to anion



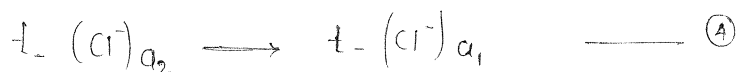
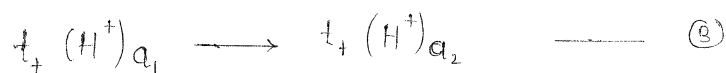
$$\Rightarrow E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{a_1}{a_2} \right) = \frac{RT}{nF} \ln \left( \frac{\gamma_1 \cdot m_1}{\gamma_2 \cdot m_2} \right) = \frac{RT}{nF} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

(v) Electrolyte Conc. Cell with transference.

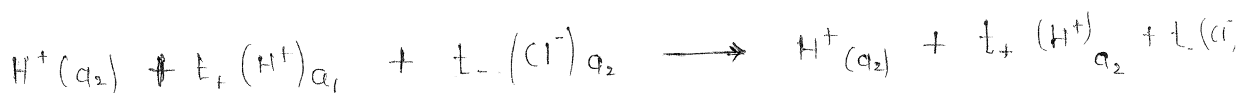
→ without salt bridge & transfer of ions take place.



A/c Faradays law, no. of ions transfer depends on their transport number



Net cell reaction :



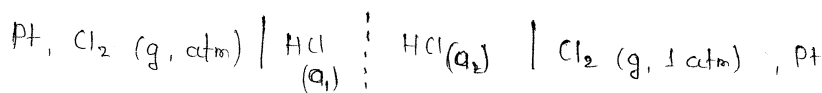


$$E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right)^{t_-}$$

$$E_{\text{cell}} = (t_-) \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right) = 2t_- \frac{RT}{nF} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1}$$

$$\text{or } E_{\text{cell}} = (t_-) \frac{RT}{nF} \ln \left\{ \frac{(a_{\pm})_2}{(a_{\pm})_1} \right\}^2 = 2t_- \frac{RT}{nF} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

Example (2)



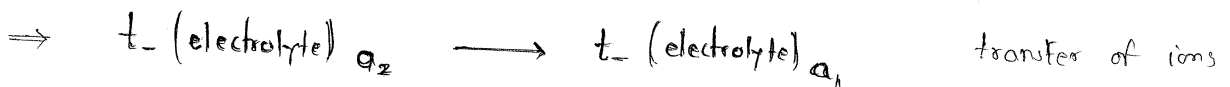
→ Electrode reverse to anion



$$E_{\text{cell}} = t_+ \frac{RT}{1 \cdot F} \ln \frac{a_1}{a_2} = 2t_+ \frac{RT}{nF} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2} = 2t_+ \frac{RT}{1 \cdot F} \ln \frac{\gamma_1 \cdot m_1}{\gamma_2 \cdot m_2}$$

Note

(i) Electrode reverse to cation.



$$\Rightarrow E_{\text{cell}} = t_- \frac{RT}{nF} \ln \frac{a_2}{a_1} = 2t_- \frac{RT}{nF} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} = 2t_- \frac{RT}{nF} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1}$$

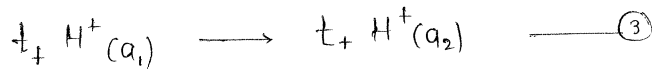
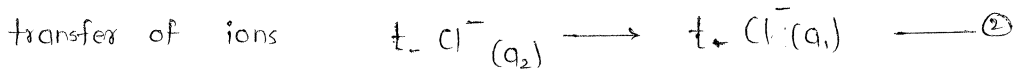
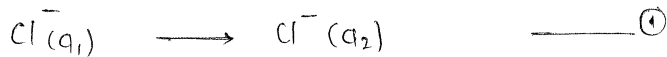
(ii) Electrode reverse to anion.



$$\Rightarrow E_{\text{cell}} = t_+ \frac{RT}{nF} \ln \frac{a_1}{a_2} = 2t_+ \frac{RT}{nF} \ln \left\{ \frac{(a_{\pm})_1}{(a_{\pm})_2} \right\}$$

$$= 2t_+ \frac{RT}{nF} \ln \left( \frac{\gamma_1 \cdot m_1}{\gamma_2 \cdot m_2} \right)$$

Example  $\rightarrow$   $\text{Ag}^+, \text{AgCl} \mid \text{Cl}^-(a_1) \parallel \text{Cl}^-(a_2) \mid \text{AgCl}, \text{Ag}$



total cell reaction : 1 + 2 + 3.



In the place of ~~HCl~~, HCl if KCl is taken, then.



A/c Nernst equation

$$E_{\text{cell}} = - \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right)^{t_+} = t_+ \frac{RT}{nF} \ln \left( \frac{a_1}{a_2} \right) = t_+ \frac{RT}{nF} \ln \left\{ \frac{(a_+)_{a_1}}{(a_+)_{a_2}} \right\}^2 = 2t_+ \frac{RT}{nF} \ln \frac{(a_+)_{a_1}}{(a_+)_{a_2}}$$

Que-1 The overall reaction for the passage of one Faraday of charge in the following cell.

Que-2 The aq. sol<sup>n</sup> of KCl is used as a salt bridge. This is because

- (i) KCl is ionic compound
- (ii) transference no. of  $K^+$  &  $Cl^-$  is nearly same.
- (iii) liquid junction potential of KCl is very high
- (iv) KCl is soluble in water.

→  $(t_+ = t_-)$  for salt bridge.

∴ option (ii) is the correct answer.

---

Que-3 The correct statement among the following is

- (i) salt bridge is required for the mixing of sol<sup>n</sup> in two half cell
- (ii) Salt bridge enhances rate of reaction.
- (iii) salt bridge allows current to flow between the half cell without mixing of solution.
- (iv) salt bridge consist of non-electrolyte in a gel.

→ option (iii) is the correct answer. because.

salt bridge completes the circuit between two half cell

---

Que-4 The overall reaction in the following cell is given by



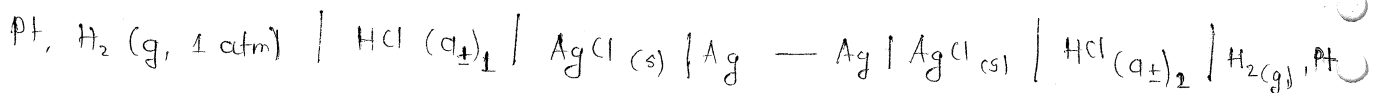
- (i)  $t_+ (KCl)_{a_2} \longrightarrow t_+ (KCl)_{a_1}$
- (ii)  $t_+ (KCl)_{a_1} \longrightarrow t_+ (KCl)_{a_2}$
- (iii)  $t_- (KCl)_{a_2} \longrightarrow t_- (KCl)_{a_1}$
- (iv)  $t_+ (KCl)_{a_1} \longrightarrow t_- (KCl)_{a_2}$

→ Electrode is reverse to anion and this Electrolyte conc. cell with transference type Galvanic cell. Therefore overall reaction is.

∴  $t_+ (KCl)_{a_1} \longrightarrow t_+ (KCl)_{a_2}$  ∴ option (ii) is the correct answer.

---

Que-5 The correct Nernst eq<sup>n</sup> for the cell reaction



$$(i) E = \frac{2RT}{F} \ln \frac{(a_{\pm})_1}{(a_{\pm})_2}$$

$$(ii) E = \frac{RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

$$(iii) E = \frac{2RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

$$(iv) E = \frac{RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}$$

→ End electrodes are reverse to cation & middle electrodes are reverse to anion.  
and this is electrolyte conc. cell without transference type Galvanic cell.

Therefore overall cell reaction is :  $\text{HCl}(a_2) \longrightarrow \text{HCl}(a_1)$

$$\therefore E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right) = \frac{RT}{nF} \ln \left\{ \frac{(a_{\pm})_2}{(a_{\pm})_1} \right\}^2 = \frac{2RT}{nF} \ln \left\{ \frac{(a_{\pm})_2}{(a_{\pm})_1} \right\}$$

∴ option (iii) is the correct answer.

Que-6 For  $\text{Pt}, \text{H}_2(p_1) \mid \text{H}^+(M) \mid \text{H}_2(p_2), \text{Pt}$ , cell reaction will be spontaneous if.

- (i)  $p_1 = p_2$       (ii)  $p_1 > p_2$       (iii)  $p_2 > p_1$       (iv)  $p_2 = 2p_1$

→ The given type of galvanic cell is electrode conc. cell and it is reverse to cation.

The overall cell reaction :  $\text{Pt}, \frac{1}{2} \text{H}_2(p_1) \longrightarrow \text{Pt}, \frac{1}{2} \text{H}_2(p_2)$

$$\therefore E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{p_1}{p_2} \right)$$

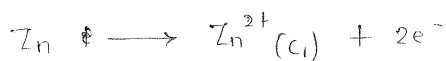
∴ above reaction become spontaneous if  $p_1 > p_2$

∴ option (ii) is the correct answer.

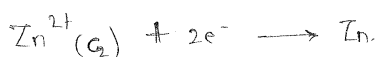
Que-7 For  $\text{Zn} \mid \text{Zn}^{2+}(C_1) \parallel \text{Zn}^{2+}(C_2) \mid \text{Zn}$ ,  $\Delta G = -ve$ , if.

- (i)  $C_1 = C_2$       (ii)  $C_2 > C_1$       (iii)  $C_1 > C_2$       (iv)  $C_1 = 2C_2$

→ The given cell is electrode conc. cell.



∴ For  $\Delta G = -ve$



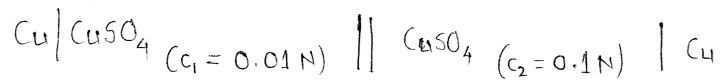
$$C_2 > C_1$$



∴ option (ii) is the correct answer

$$\therefore E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{C_2}{C_1} \right)$$

Que-8 Calculate the emf of the following cell at 298 K



(i) 2.95 V

(ii) 0.295 V.

(iii) 0.0295 V

(iv) 5.90 V.

→ This is Electrode conc. cell.

$$E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{c_2}{c_1} \right)$$

$$\therefore E_{\text{cell}} = +0.0295 \text{ V.}$$

$$= \frac{0.059}{2} \log \left( \frac{100}{10} \right)$$

\(\therefore\) option (iii) is the correct answer.

$$= +0.0295 \log 10$$

Que-9 Calculate emf of the following cell at 25°C.



the  $(\gamma_{\pm})$  of the electrolyte will be assumed to be unity

→ Given galvanic cell is electrode ~~potential~~ concentration cell.

$$E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{a_2}{a_1} \right)$$

$$= \frac{0.059}{2} \log \left( \frac{0.1}{0.01} \right)$$

$$= 0.0295 \log \left( \frac{10}{1} \right)$$

$$= 0.0295 \times \log 10$$

$$= 0.0295 \times 1$$

$$= 0.0295$$

# Liquid Junction potential ( $E_J$ ) : excess potential developed due to transfer of ions

$$\rightarrow E_{w.o.t} = E_{\text{cathode}} - E_{\text{anode}} \quad \leftarrow (\text{red}^n \text{ potential})$$

$$E_{w.t} = E_{\text{cathode}} - E_{\text{anode}} + E_J$$

$$\therefore \boxed{E_J = E_{w.t} - E_{w.o.t}}$$

Example (1)



$$E_J = ?$$

$$t_J = t_{w.t} - t_{w.o.t.}$$

$$= 2t_- \frac{RT}{nF} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1} - \frac{RT}{1 \cdot F} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1}$$

$$= \frac{RT}{1 \cdot F} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1} (2t_- - 1)$$

$$= \frac{RT}{1 \cdot F} \ln \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1} (2t_- - t_+ - t_-)$$

$$E_J = (t_- - t_+) \frac{RT}{1 \cdot F} \ln \left( \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1} \right)$$

(i) If  $t_+ = t_- \Rightarrow E_J = 0$  (for salt bridge  $E_J = 0$ ).

(ii) liquid junction potential  $E_J$  arises when there is difference between the speed of cation and anions.

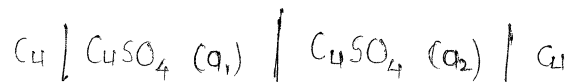
Note (i) Electrode reverse to cation.

$$\Rightarrow E_J = (t_- - t_+) \frac{RT}{nF} \ln \left( \frac{\gamma_2 \cdot m_2}{\gamma_1 \cdot m_1} \right)$$

(ii) Electrode reverse to anion.

$$\Rightarrow E_J = (t_+ - t_-) \frac{RT}{nF} \ln \left( \frac{\gamma_1 \cdot m_1}{\gamma_2 \cdot m_2} \right)$$

Example ①



$$\rightarrow E_J = (t_{\text{SO}_4^{2-}} - t_{\text{Cu}^{2+}}) \frac{0.059}{2} \log \left( \frac{a_2}{a_1} \right)$$

Example ②  $\text{Cl}_2 (g, 1 \text{ atm}) \mid \text{HCl} (a_1) \mid \text{HCl} (a_2) \mid \text{Cl}_2 (g, 1 \text{ atm})$

$$\rightarrow E_J = (t_{\text{H}^+} - t_{\text{Cl}^-}) \frac{0.059}{1} \log \left( \frac{a_1}{a_2} \right)$$

Example ③  $\text{Pb, PbSO}_4 \mid \text{CuSO}_4 (a_1) \parallel \text{CuSO}_4 (a_2) \mid \text{PbSO}_4, \text{Pb}$ .

→ Electrode is reverse to anion.

$$E_T = (t_+ - t_-) \frac{RT}{2F} \ln \left( \frac{a_1}{a_2} \right) = (t_+ - t_-) \frac{0.059}{2} \log \left( \frac{a_1}{a_2} \right)$$

### # Determination of transport numbers -

(i) transport number of cation.

$$2t_+ = \frac{E_{wt}}{E_{wot}}$$

(ii) transport number of anion.

$$2t_- = \frac{E_{wt}}{E_{wot}}$$

### # Kohlrausch's law of independent migration of ion.

Electrolyte at  $\infty$  dilution or 0% conc. where 100% dissociation of electrolyte at that situation, each ion makes a definite contribution towards total conductance irrespective of other ion present.

Ex: NaCl at  $\infty$  dilution

$$\begin{array}{ccc} \lambda_{\infty} & = & \lambda_{\text{Na}^+}^{\infty} + \lambda_{\text{Cl}^-}^{\infty} \\ \downarrow & & \downarrow \quad \downarrow \\ 100 \text{ unit} & & 60 \text{ unit} \quad 40 \text{ unit.} \end{array}$$

Even in presence of  $\text{Br}^-$  or  $\text{SO}_4^{2-}$  or  $\text{NO}_3^-$

$\lambda_{\text{Na}^+}^{\infty}$  is always 60 unit.

$$\begin{array}{ccc} \lambda_{\text{NaBr}}^{\infty} & \longrightarrow & \lambda_{\text{Na}^+}^{\infty} + \lambda_{\text{Br}^-}^{\infty} \\ \downarrow & & \downarrow \quad \downarrow \\ 90 \text{ u} & & 60 \text{ u} \quad 30 \text{ unit} \end{array}$$

$$\begin{array}{ccc} \lambda_{\text{KCl}}^{\infty} & \longrightarrow & \lambda_{\text{K}^+}^{\infty} + \lambda_{\text{Cl}^-}^{\infty} \\ \downarrow & & \downarrow \quad \downarrow \\ 110 \text{ unit.} & & 70 \text{ unit} \quad 40 \text{ unit} \end{array}$$

$$\begin{array}{ccc} \lambda_{\text{KBr}}^{\infty} & \longrightarrow & \lambda_{\text{K}^+}^{\infty} + \lambda_{\text{Br}^-}^{\infty} \\ \downarrow & & \downarrow \quad \downarrow \\ 100 \text{ unit} & & 70 \text{ unit} \quad 30 \text{ unit} \end{array}$$



$$\lambda_{\infty} = \lambda_+ + \lambda_-$$

$\lambda$  - equivalent conductance  
 $\lambda_c \neq \lambda$

$$\lambda_{\infty} = \lambda_{\text{cation}} + \lambda_{\text{anion}}$$

$$\Lambda_{\infty} = \lambda_{\text{cation}} n_{\text{cation}} + \lambda_{\text{anion}} n_{\text{anion}}$$

where  $\lambda_c$  - molar conductance of cation  
 $n_c$  - no. of cation  
 $n_a$  - no. of anion  
 $\lambda_a$  - molar conductance of anion

$$\Lambda_{\infty} = \lambda_c n_c + \lambda_a n_a$$



$$n_c = 1 \quad n_a = 1$$

$$\Lambda_{\infty} = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-}$$



$$n_c = 1 \quad n_a = 2$$

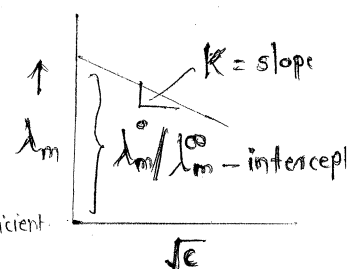
$$\Lambda_{\infty} = \lambda_{\text{Ba}^{2+}} + 2\lambda_{\text{Cl}^-}$$

Kohlrausch's equation: Since strong electrolyte weakly depends on conc., so Kohlrausch proposed eqn which gives relation between molar conductance &  $\sqrt{c}$

$$\lambda_m = \lambda_m^{\circ} / \lambda_m^{\infty} - K\sqrt{c}$$

$\lambda_m^{\circ} / \lambda_m^{\infty}$  - molar conductance at zero conc. or  $\infty$  dilut<sup>n</sup>

$K$ : Kohlrausch's constant / Kohlrausch's Coefficient



⇒ Application of Kohlrausch's law.

$$\lambda_c = \lambda_c^{\infty} - K\sqrt{c} \quad \lambda_c - \text{molar conductance.}$$

(i) relation between transport no. & equivalent conductance.

$$\lambda_{\text{ion}} \propto v_{\text{ion}}$$

$$\lambda_c \propto v_c \quad \text{--- ①}$$

$$\lambda_a \propto v_a \quad \text{--- ②}$$

$$\lambda_c + \lambda_a \propto (v_c + v_a)$$

where  $v$  is velocity

$v_{\text{ion}}$  - velocity of ion

A/c Kohlrausch's law:  $\lambda_{\infty} \propto (\lambda_c + \lambda_a)$

dividing ① by eq<sup>n</sup> ③

dividing eq<sup>n</sup> ② by eq<sup>n</sup> ③

$$\frac{\lambda_c}{\lambda_{\infty}} = t_c$$

$$\frac{\lambda_a}{\lambda_{\infty}} = t_a$$

$$\therefore \lambda_c = \lambda_{\infty} \cdot t_c$$

$$\lambda_a = \lambda_{\infty} \cdot t_a$$

In general:

$$\lambda_{\text{ion}} = \lambda_{\infty} t_{\text{ion}}$$

$$t_{\text{ion}} = \frac{\lambda_{\text{ion}}}{\lambda_{\infty}}$$

Example ①  $\lambda_{\text{H}^+} = t_{\text{H}^+} \cdot \lambda_{\infty}(\text{HCl})$

$$\lambda_{\text{OH}^-} = t_{\text{H}^+} \cdot \lambda_{\infty}(\text{NaOH})$$

(ii) Determination of  $\lambda_{\infty}$  of weak electrolyte.

Example ①  $\lambda_{\infty}(\text{CH}_3\text{COO}^-\text{H}^+) \rightarrow \lambda_{\infty}$  of 3 strong electrolyte  
 $\text{CH}_3\text{COO}^-\text{Na}^+, \text{H}^+\text{Cl}^-, \text{NaCl}$

$\lambda_{\infty}$  (weak electrolyte) cannot be calculated experimentally, w/c Kohlrausch's law, it can be calculated by taking 3  $\lambda_{\infty}$  (strong electrolyte)

$$\lambda_{\infty}(\text{CH}_3\text{COO}^-\text{Na}^+) = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{Na}^+} \quad \text{--- ①}$$

$$\lambda_{\infty}(\text{H}^+\text{Cl}^-) = \lambda_{\text{H}^+} + \lambda_{\text{Cl}^-} \quad \text{--- ②}$$

$$\lambda_{\infty}(\text{Na}^+\text{Cl}^-) = \lambda_{\text{Na}^+} + \lambda_{\text{Cl}^-} \quad \text{--- ③}$$

$$1 + 2 - 3$$

$$\lambda_{\text{CH}_3\text{COO}^-} + \cancel{\lambda_{\text{Na}^+}} + \lambda_{\text{H}^+} + \cancel{\lambda_{\text{Cl}^-}} - \cancel{\lambda_{\text{Na}^+}} - \cancel{\lambda_{\text{Cl}^-}} = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+}$$

$$= \lambda_{\infty}(\text{CH}_3\text{COOH})$$

$$\therefore \lambda_{\infty}(\text{CH}_3\text{COOH}) = \lambda_{\infty}(\text{CH}_3\text{COONa}) + \lambda_{\infty}(\text{HCl}) - \lambda_{\infty}(\text{NaCl})$$

Example ②  $\lambda_{\infty}(\text{NH}_4\text{OH})$

$\rightarrow \text{NH}_4\text{Cl}, \text{NaOH}, \text{NaCl}$

$$\lambda_{\infty}(\text{NH}_4\text{OH}) = \lambda_{\infty}(\text{NH}_4\text{Cl}) + \lambda_{\infty}(\text{NaOH}) - \lambda_{\infty}(\text{NaCl})$$

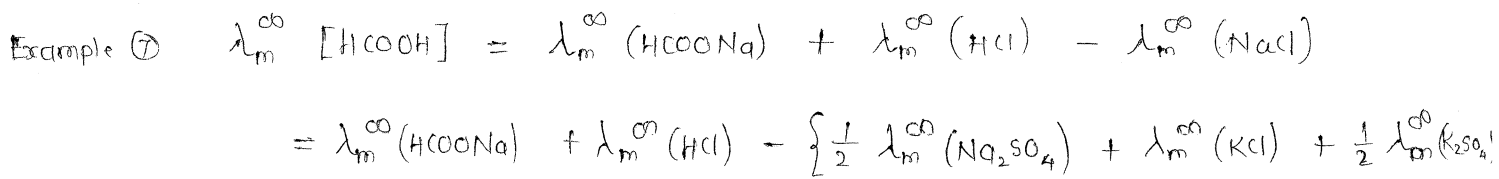
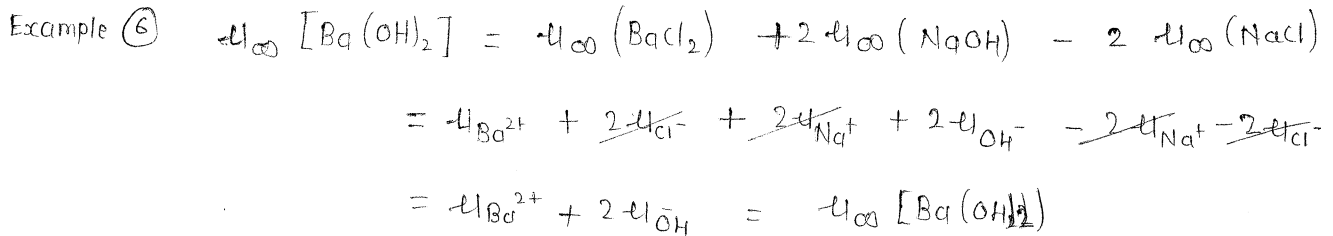
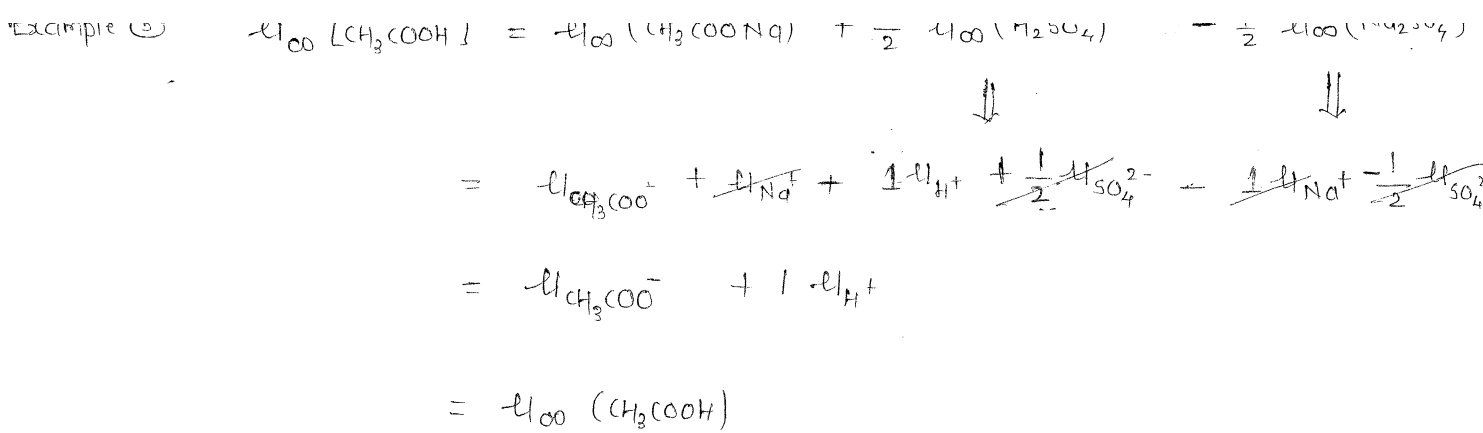
Example ③  $\lambda_{\infty}[\text{Ba}(\text{OH})_2]$

$$\rightarrow \lambda_{\infty}[\text{Ba}(\text{OH})_2] = \lambda_{\infty}(\text{BaCl}_2) + \lambda_{\infty}(\text{KOH}) - \lambda_{\infty}(\text{KCl})$$

$$\begin{array}{ccc} \downarrow & & \downarrow \\ \lambda_{\text{Ba}^{2+}} + \lambda_{\text{Cl}^-} & + & \lambda_{\text{K}^+} + \lambda_{\text{OH}^-} - \lambda_{\text{K}^+} - \lambda_{\text{Cl}^-} \end{array}$$

Example ④  $\lambda_{\infty}[\text{CH}_3\text{COOH}] = \lambda_{\infty}[\text{CH}_3\text{COONa}] + \lambda_{\infty}[\text{H}_2\text{SO}_4] - \lambda_{\infty}[\text{Na}_2\text{SO}_4]$

$$\begin{aligned} & \downarrow \\ & = \lambda_{\text{CH}_3\text{COO}^-} + \cancel{\lambda_{\text{Na}^+}} + \lambda_{\text{H}^+} + \lambda_{\text{SO}_4^{2-}} - \cancel{\lambda_{\text{Na}^+}} - \lambda_{\text{SO}_4^{2-}} \\ & = \lambda_{\text{CH}_3\text{COO}^-} + \lambda_{\text{H}^+} \\ & = \lambda_{\infty}(\text{CH}_3\text{COOH}) \end{aligned}$$



(iii) Determination of solubility of sparingly soluble salt.

sparingly soluble salt : solubility is very very low.

: AgCl, AgBr, PbCl<sub>2</sub>, PbSO<sub>4</sub>, etc.

Example : 100 molecules of AgCl  $\longrightarrow$  5 dissociates  
95 remains undissociated



$$\lambda = \frac{1000K}{C_N} \quad C_N = \text{solubility of AgCl in gm. eq. per litre} = S$$

$\lambda = \lambda_{\infty}$  on dilution.

$$\lambda_{\infty} = \frac{1000K}{S}$$

$$\left[ S = \frac{1000K}{\lambda_{\infty}} \right] \text{ gm. eq. L}^{-1} \longrightarrow \text{solubility in gram. eq. / Litre}$$

$$n_{\text{gm. eq.}} = \frac{W}{\text{eq. wt.}}$$

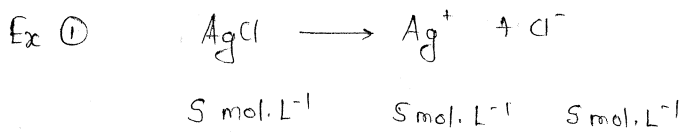
$$W = n_{\text{gm. eq.}} \times \text{eq. wt.}$$

$$\therefore \boxed{S = \frac{1000 K}{\lambda_{\infty}} \times \text{Eq. wt.}} \quad \text{gram/Litre.} \quad \text{--- solubility in gram/L}$$

$$\boxed{S = \frac{1000 K}{\lambda_{\infty}} \text{ mol/L}^{-1}}$$

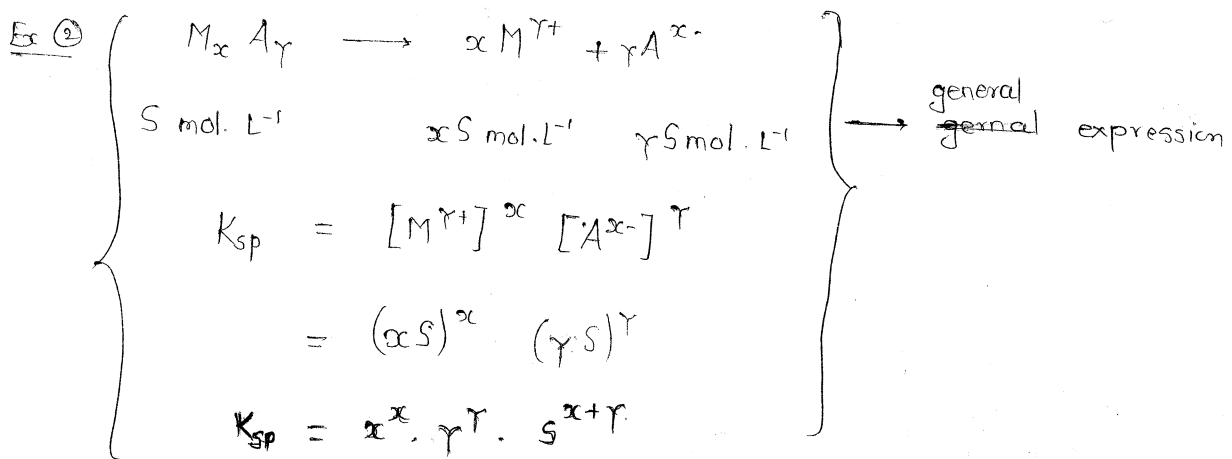
# Solubility product ( $K_{sp}$ )

$$\boxed{K_{sp} = x^x \cdot \gamma^{\gamma} \cdot s^{(x+\gamma)}}$$



$$K_{sp}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-]$$

$$= s^2$$



Ex ①  $K_{sp}(\text{AgBr}) = 1^1 \cdot 1^1 \cdot s^{1+1} = s^2 \quad x=1, \gamma=1$

②  $K_{sp}(\text{BaCl}_2) = 1^1 \cdot 2^2 \cdot s^{1+2} = 4s^3 \quad x=1, \gamma=2$

③  $K_{sp}[\text{Al}_2(\text{SO}_4)_3] = 2^2 \cdot 3^3 \cdot s^{2+3} = 4 \times 27 s^5 = 108 s^5 \quad x=2, \gamma=3$

{ At given temperature, solubility product of electrolyte is constant is called solubility product principle. }

→ Ionic product  $> K_{sp}$  : supersaturated sol.  
: some ions are precipitated

→ Ionic product  $< K_{sp}$  : unsaturated solution  
: more ions required to saturate the solution.

→ Ionic product  $= K_{sp}$  : saturated solution.

### # Potentiometric titration - potentiometer.

→ Determine end point based on cell potential values by using potentiometer.

→ principle : electrode potential is depends upon conc. of electrolyte.

#### Advantages

(i) No indicator required.

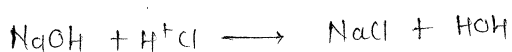
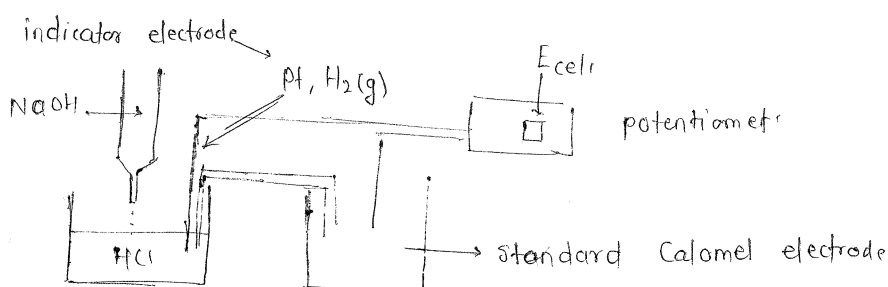
(ii) applicable to coloured solution / electrolyte also.

\*\*\* (iii) No indicator is available for W.A. vs W.B titration by volumetric titration. Hence potentiometric titrations are used for W.A vs W.B titration.

(iv) Accurate results obtain compared to volumetric titration.

→ We have to select an electrode reverse to ion, whose conc. is changing during titration.

Ex (i) : Acid - base titration.



⇒  $H^+$  ion conc. is changing

Ex ② precipitation titration

Quinhydrone, Hydrogen, glass electrode all are sensible / reverse to  $H^+$  ion.



$Ag^+$  ion conc. changes during titration.

⇒ Application of potentiometric titration.

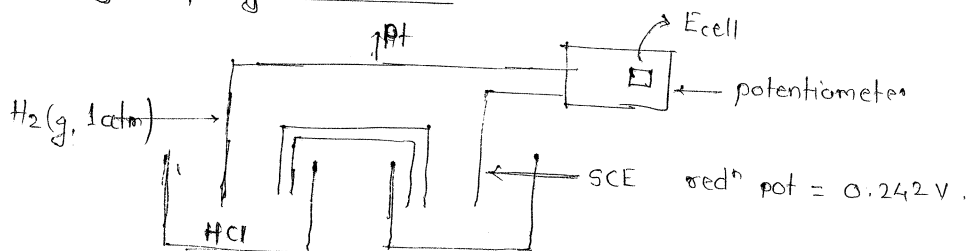
(i) Determination of pH

$$pH = -\log [H^+]$$

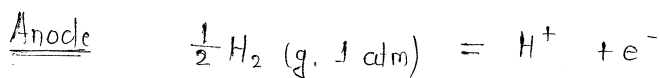
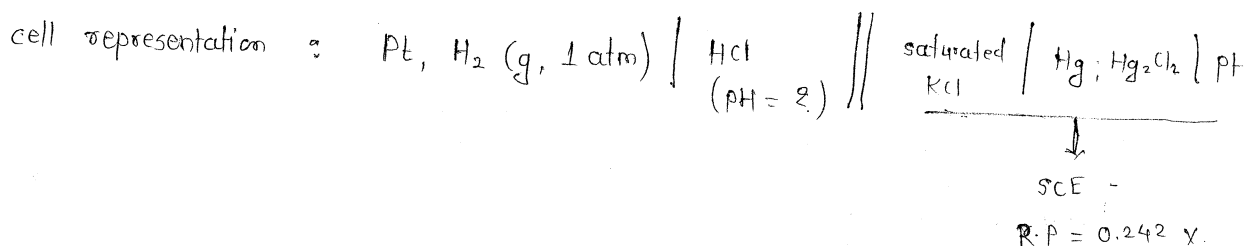
↓  
electrode reverse to  $H^+$  ion.

- ↓
- $H_2$ , Pt electrode
- quinhydrone electrode
- glass electrode.

② by using Hydrogen electrode.



$$pH = ?$$



$$E_{H_2/H^+} = E_{H_2/H^+}^\circ - \frac{0.059}{1} \log [H^+]$$

$$E_{H_2/H^+} = +0.059 pH. \quad \text{--- oxidn potential } (\because pH = -\log [H^+])$$

$E_{H^+/H_2} = -0.059 pH.$

--- reduction potential

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

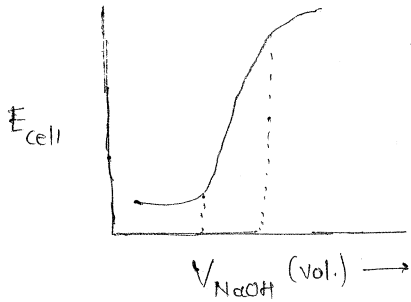
$$E_{\text{cell}} = 0.242 + 0.059 \text{ pH}$$

$$\text{pH} = \frac{E_{\text{cell}} - 0.242}{0.059}$$

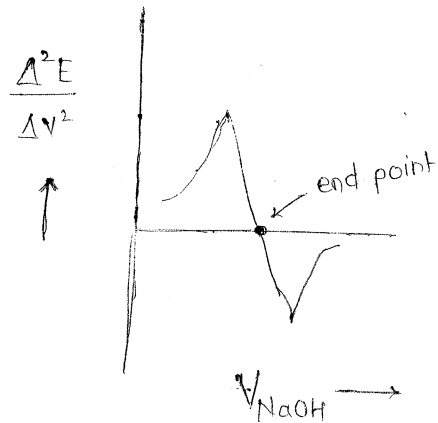
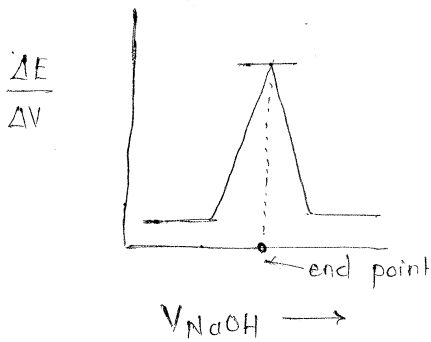
→ general expression.

$$\text{pH} = \frac{E_{\text{cell}} - E_{\text{cathode}}}{0.059} = \frac{\text{End point} - E_{\text{cathode}}}{0.059}$$

(ii) Acid-base titration.

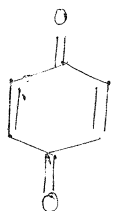


During addition of NaOH, cell potential ↑ slowly in the beginning and sudden jump in the potential is observe.

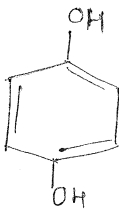


(b) by using quinhydrone electrode

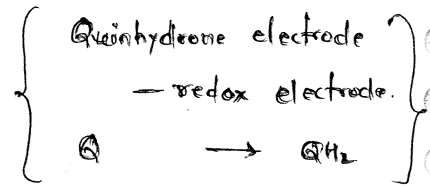
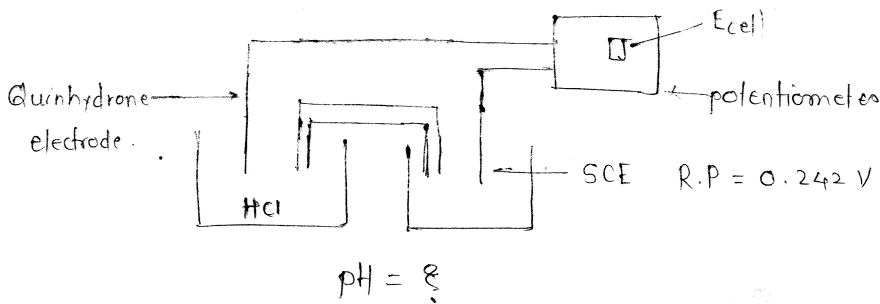
Quinhydrone : equimolar mixture of quinone & hydroquinone.  
[1:1]



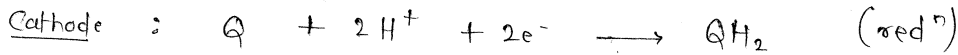
Quinone  
(Q)



hydroquinone  
(QH<sub>2</sub>)



$$\left( E_{Q/QH_2}^{\circ} = 0.699 \text{ V} \right)$$



$$E_{Q/QH_2} = E_{Q/QH_2}^{\circ} - \frac{0.059}{2} \log \frac{1}{[H^+]^2}$$

$$E_{Q/QH_2} = 0.699 + \frac{0.059}{2} \log [H^+]^2$$

$$E_{Q/QH_2} = 0.699 + \frac{0.059}{2} \times 2 \log [H^+]$$

$$E_{Q/QH_2} = 0.699 - 0.059 \text{ pH}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad - E_{\text{cell}} = 0.699 - E_{\text{anode}} = -0.059 \text{ pH}$$

$$= E_{Q/QH_2} - E_{\text{SCE}}$$

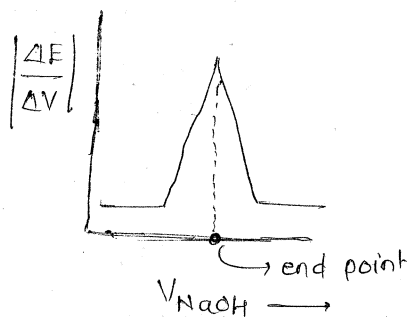
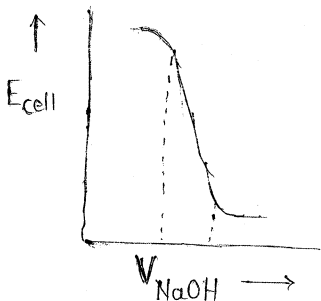
$$= 0.699 - 0.059 \text{ pH} - 0.242$$

$$\text{pH} = \frac{0.699 - E_{\text{cell}} - E_{\text{anode}}}{0.059}$$

$$E_{\text{cell}} = 0.457 - 0.059 \text{ pH}$$

$$\therefore \text{pH} = \frac{0.457 - E_{\text{cell}}}{0.059}$$

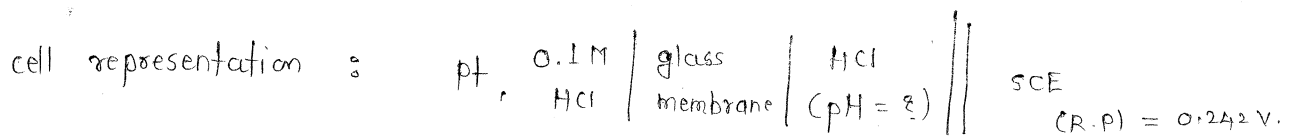
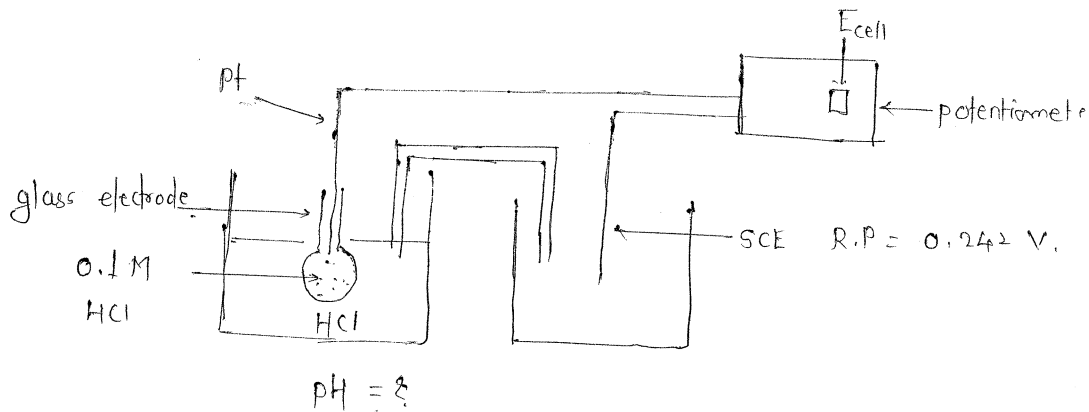
Acid-base titration - During NaOH addition, cell potential decreases slowly and the sudden decrease is observed at end point.





(c) by using glass electrode

When a thin glass membrane is in contact with two solutions of different pH, some potential is developed at interface of glass & solution & this potential depends on difference in pH of those two solutions.



$$E_g = E_g^\circ - 0.059 \text{pH}$$

$E_g^\circ$  - depends on type of glass or nature of glass

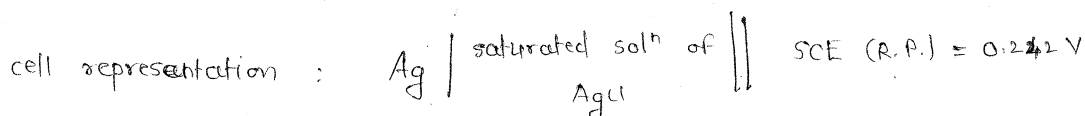
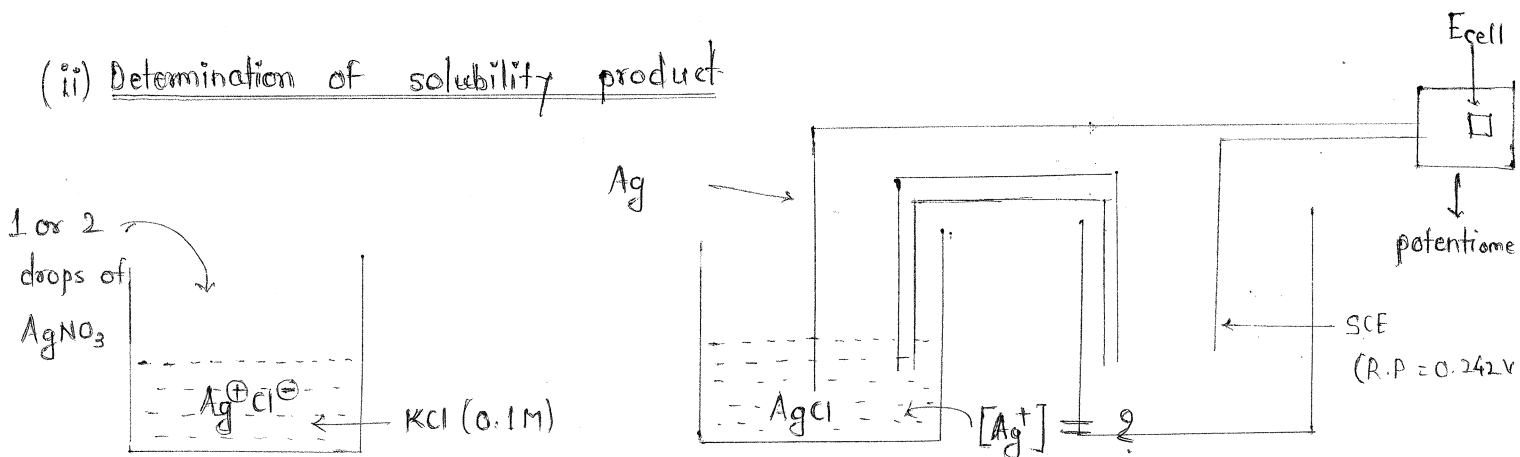
$$E_{\text{cell}} = 0.242 - E_g$$

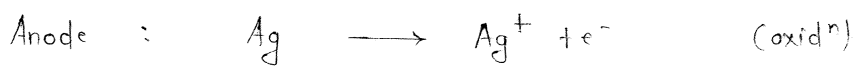
$E_g^\circ$  - standard glass electrode potential can be determined by taking a solution of known pH.

$$E_{\text{cell}} = 0.242 - E_g^\circ + 0.059 \text{pH}$$

$$\therefore \text{pH} = \frac{E_{\text{cell}} + E_g^\circ - 0.242}{0.059}$$

(ii) Determination of solubility product





$$E_{\text{Ag}|\text{Ag}^+} = E_{\text{Ag}|\text{Ag}^+}^{\circ} - \frac{0.059}{1} \log [\text{Ag}^+] \quad \text{--- oxid}^n \text{ potential}$$

$$E_{\text{Ag}|\text{Ag}^+} = -0.80 - 0.059 \log [\text{Ag}^+]$$

$$E_{\text{Ag}^+|\text{Ag}} = 0.80 + 0.059 \log [\text{Ag}^+] \quad \text{--- red}^n \text{ potential}$$

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{SCE}} - E_{\text{Ag}^+|\text{Ag}}$$

$$= 0.242 - 0.80 - 0.059 \log [\text{Ag}^+]$$

$$= -0.558 - 0.059 \log [\text{Ag}^+]$$

$$\log [\text{Ag}^+] = - \left( \frac{E_{\text{cell}} + 0.558}{0.059} \right)$$



(S)

then  $s = \gamma [\text{Cl}^-]$



$$\log [\text{Ag}^+] = - \left( \frac{E_{\text{cell}} + 0.558}{0.059} \right) \implies \text{if } [\text{Ag}^+] = \gamma$$

Que-1 At  $27^\circ\text{C}$  the  $E_{\text{cell}}$  of the following cell is  $0.029\text{ V}$ .

$\text{Ag}, 0.1\text{ M KCl} \mid \text{saturated sol}^n \text{ AgCl} \parallel \text{SCE}$ . Find the solubility product

$$\left( E_{\text{Ag}^+|\text{Ag}}^{\circ} = 0.80\text{ V} \quad \& \quad E_{\text{SCE}} = 0.242\text{ V} \right)$$

- (i)  $10^{-19}$       (ii)  $10^{-10}$       (iii)  $10^{-1}$       (iv)  $10^{-8}$

$$\implies \log [\text{Ag}^+] = - \left( \frac{E_{\text{cell}} + 0.558}{0.059} \right) = - \left( \frac{0.029 + 0.558}{0.059} \right) = - \frac{0.587}{0.059} = -9.94 \approx -10$$

$$\log [\text{Ag}^+] = -10$$

$$\therefore [\text{Ag}^+] = 10^{-10}$$

$$\therefore \boxed{K_{\text{sp}} = 10^{-20}} \approx 10^{-19}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

$$= 10^{-10} [\text{Cl}^-]$$

$$= 10^{-10} \times 10^{-10}$$

$\therefore$  option (i) is the correct answer

$$\text{solubility } s = [\text{Ag}^+] = 10^{-10}$$

the pH of solution.



$$\text{pH} = \frac{E_{\text{cell}} / \text{End point} - E_{\text{cathode}}}{0.059}$$

$$\text{pH} = \frac{0.236 \text{ V} - 0}{0.059} = \frac{0.236}{0.059} = \frac{23.6}{6}$$

$$\boxed{\text{pH} = 3.93}$$

conc. = 1 M

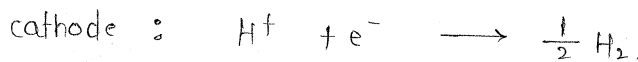
standard Hydrogen electrode

$E_{\text{cathode}} = 0$  (R.P)

Que-3 The potential of following cell at  $25^\circ\text{C}$  is  $0.118 \text{ V}$ . Then calculate pH.



$$\text{pH} = \frac{E_{\text{cell}} - E_{\text{cathode}}}{0.059}$$



A/c Nernst eq<sup>n</sup>

$$E_{\text{H}^+/\text{H}_2} = - \frac{0.059}{1} \log \frac{1}{[\text{H}^+]}$$

$$E_{\text{H}^+/\text{H}_2} = - 0.059 \log \left( \frac{1}{0.1} \right)$$

$$E_{\text{H}^+/\text{H}_2} = -0.059 \log 10$$

$$E_{\text{H}^+/\text{H}_2} = -0.059 \text{ V}$$

$$\text{pH} = \frac{0.118 - (-0.059)}{0.059} = \frac{0.177}{0.059} = 3$$

$$\therefore \boxed{\text{pH} = 3}$$

Que-4 equivalent conductance of saturated  $\text{BaSO}_4$  is  $\lambda_{\infty} = 400 \text{ } \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$

and specific conductance  $K$  is  $8 \times 10^{-5} \text{ } \Omega^{-1} \text{ cm}^{-1}$ . Find the  $K_{\text{sp}}$  of

$\text{BaSO}_4$

$$(i) 4 \times 10^{-8} \text{ M}^2$$

$$(ii) 2 \times 10^{-4} \text{ M}^2$$

$$(iii) 1 \times 10^{-8} \text{ M}^2$$

$$(iv) 1 \times 10^{-4} \text{ M}^2$$

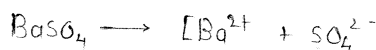
→

$$S = \frac{1000 \text{ K}}{\lambda_{\infty}} \text{ gm.eq./l.}$$

$$S = \frac{1000 \times 8 \times 10^{-5}}{4 \times 10^{-2}}$$

$$S = 2 \times 10^{-3} \times 10^{-7}$$

$$S = 2 \times 10^{-4} \text{ gm.eq./L}$$



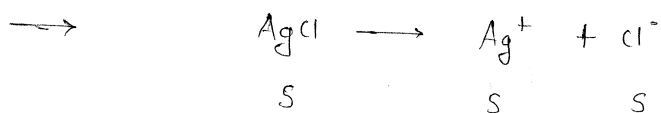
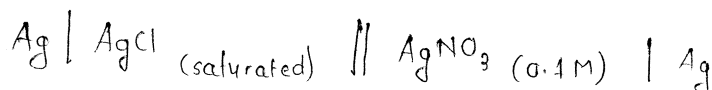
$$x=1 \quad y=1$$

$$K_{sp} = S^{1+1} = S^2$$

$$\therefore K_{sp}(\text{BaSO}_4) = S^2 = (2 \times 10^{-4} \text{ M})^2 \\ = 4 \times 10^{-8} \text{ M}^2$$

$\therefore$  option (i) is the correct answer.

Que-5 The potential of following cell at  $25^\circ\text{C}$  is  $0.236 \text{ V}$ . Calculate the solubility of  $\text{AgCl}$ .



$$\log [\text{Ag}^+] = - \left( \frac{E_{\text{cell}} + 0.858}{0.059} \right) = - \left( \frac{0.236 + 0.558}{0.059} \right) = - \left( \frac{0.794}{0.059} \right) = - \frac{794}{59} = -13.5$$

$$\log [\text{Ag}^+] = -13.5 \implies [\text{Ag}^+] = S = 10^{-13.5}$$

$$\therefore K_{sp} = (10^{-13.5})^2 = 10^{-27}$$

Que-6 The quinhydrone electrode was combined with SCE to determine pH value of given soln. the emf of solution was found to be  $0.109 \text{ V}$  at  $25^\circ\text{C}$ . calculate pH

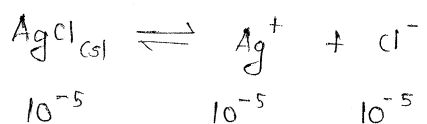
$$\rightarrow \text{pH} = \frac{0.457 - E_{\text{cell}}}{0.059} = \frac{0.457 - 0.109}{0.059} = \frac{0.354}{0.059} = \frac{354}{59}$$

$$\text{pH} = 6$$

Que-7  $S_{\text{AgCl}}$  in water at certain temp is  $10^{-5} \text{ mol.L}^{-1}$ . What is its solubility in  $0.04 \text{ M}$   $\text{KCl}$  soln at the same temp.

$$\rightarrow S = 10^{-5} \text{ mol.L}^{-1} = 10^{-5} \text{ M}$$

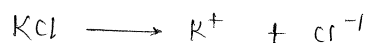
$$K_{sp} = S^2 = 10^{-10} \text{ M}^2$$



$$10^{-5}$$

$$10^{-5}$$

$$10^{-5}$$



$$S$$

$$0.04 \text{ M}$$

$$0.01 \text{ M}$$

$$0.01 \text{ M}$$

∴ solubility ↓



$10^{-5}$  → negligible value compared to  $10^{-2}$

$$\therefore [\text{Cl}^-] = 10^{-2}$$

A/c solubility product principle

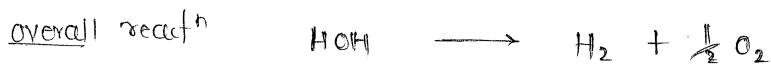
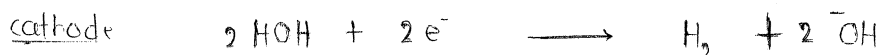
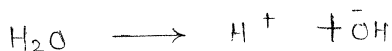
$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$10^{-10} = [\text{Ag}^+] \times 10^{-2}$$

$$[\text{Ag}^+] = 10^{-8} \text{ M.} \implies S = 10^{-8} \text{ M.}$$

Electrolysis of water.

☆☆☆



∴ For electrolysis of 1 mole of water, required 2F (2 moles of  $e^-$ ) current

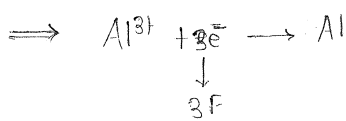
∴ Electrolysis of 1 mole of water gives 2 grams of  $\text{H}_2$  or 22.4 L of  $\text{H}_2$  under STP condition, and 16 grams of  $\text{O}_2$  or 11.2 L of  $\text{O}_2$  under STP.

$$W_{\text{H}_2} : W_{\text{O}_2} \implies 2 : 16 \implies 1 : 8$$

$$V_{\text{H}_2} : V_{\text{O}_2} \implies 22.4 : 11.2 \implies 2 : 1$$

Que-1 How much charge is required in Coulombs

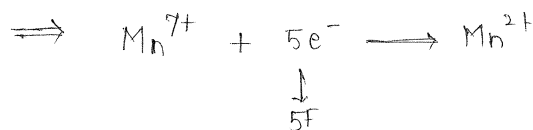
(i) to reduce  $\text{Al}^{3+}$  (1 mole) to Al



1 mole  $\text{Al}^{3+}$  — required 3F

$$\therefore \text{Charge in C} = 3 \times 96,500 \text{ C}$$
$$= 289,500 \text{ C}$$

(ii) to reduce 1 mole  $\text{MnO}_4^-$  to  $\text{Mn}^{2+}$



1 mole  $\text{Mn}^{7+}$  to  $\text{Mn}^{2+}$  — required 5F

$$= 5 \times 96,500 \text{ C}$$

$$= 482,500$$

$$= 4,82,500 \text{ C}$$

(iii) oxidized 1 mole  $H_2O$  to  $O_2$ .



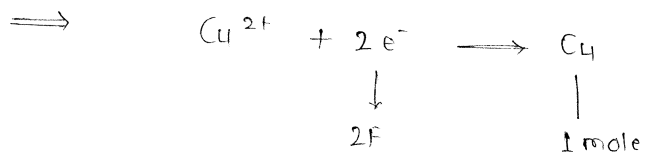
1 mole HOH required 2F

$$= 2 \times 96,500 C = 1,93,000 C$$

Questions based on Faraday's Law

Que-2 No. of Faraday required to deposit 1 mole of Cu are

- (i) 1 (ii) 2 (iii) 3 (iv) 4



$\therefore$  2F required  $\rightarrow$  to deposit 1 mole of Cu

$\therefore$  option (ii) is the correct answer.

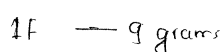
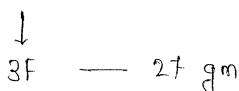
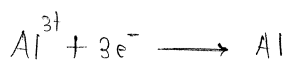
Que-3 What is the weight of Al deposited at by passing a current of 965 Amp. in 10 sec.

$$\Rightarrow I = 965 \text{ Amp}, t = 10 \text{ sec}, \text{Eq. wt of Al} = \frac{27}{3} = 9 \text{ gram}, w = ?$$

$$w = \frac{It \times \text{eq. wt}}{1F}$$

$$= \frac{965 \times 10 \times 9}{96500} = \frac{90}{100}$$

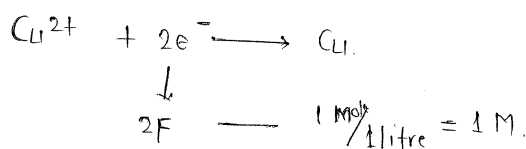
$$= 0.9 \text{ grams}$$



$\therefore$  0.9 gram of Al deposited by 965 Amp in 10 sec.

Que-4 1 litre of 1 M  $CuSO_4$  sol<sup>n</sup> is electrolysed. After passing 2F charge. The molarity of  $CuSO_4$  will be.

- (i) M/2 (ii) M/4 (iii) M (iv) zero.



By passing 2F current 1 mole/litre of  $Cu^{2+}$  will be deposited

$\therefore$  remaining  $Cu^{2+} = 0$ /litre.

$\therefore$  molarity become Zero after passing 2F charge.

$\therefore$  option (4) is the correct answer.

Que-5 For electrosynthesis of a substance.

(i)  $\Delta G = +ve$ ,  $\Delta E = -ve$  (ii)  $\Delta G = -ve$ ,  $E = +ve$

(iii)  $\Delta G = +ve$ ,  $E = +ve$  (iv)  $\Delta G = -ve$ ,  $E = -ve$

$\Rightarrow$  Electrosynthesis  $\equiv$  Non-spontaneous process  $\Rightarrow \Delta G = +ve$  -  $\Delta G = -nFE$ ,  $E = -ve$

$\therefore$  option (i) is the correct answer.

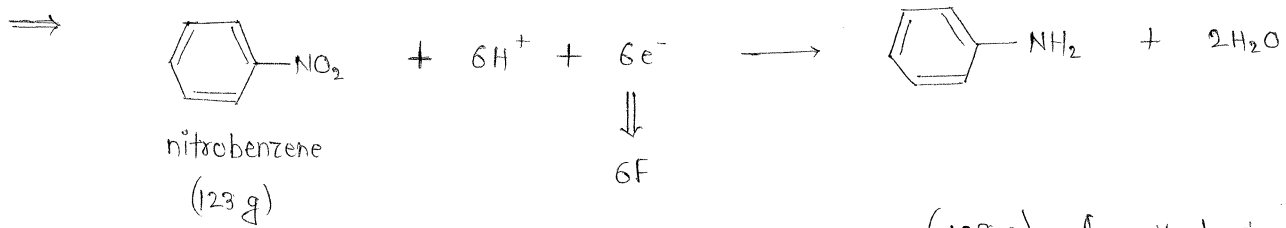
Que-6 Which of the following has maximum conductivity.

- (i)  $[Cr(NH_3)_6]Cl_3$  (ii)  $[Cr(NH_3)_3Cl_3]$  (iii)  $[Cr(NH_3)_5Cl]Cl$  (iv)  $[Cr(NH_3)_4Cl_2]Cl$

$\therefore [Cr(NH_3)_6]Cl_3 \longrightarrow$  produces 4 ions more than other compound

$\therefore$  option (1) is the correct answer.

Que-7 The quantity of electricity ~~reduce~~ required to reduce 12.3 g of nitrobenzene to aniline in acid medium is.



6 F  $\longrightarrow$  required to reduce 1 mole (123 g) of nitrobenzene

$x$  F  $\longrightarrow$  required to reduced 0.1 mole (12.3 g) of nitrobenzene

$$x = \frac{6 \times 12.3}{123} = \frac{6}{10} = 0.6 F$$

$\therefore 0.6 F = 0.6 \times 96500 \text{ C}$  electricity is required to reduced 12.3 g of nitrobenzene.

Que-8 An electrolytic cell consists of  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$  &  $\text{CuSO}_4$  in aqueous sol<sup>n</sup>.

When some electricity is passed through that sol<sup>n</sup> the product initially formed at anode and cathode respectively are.

$\Rightarrow$  cations formed :  $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{H}^+$       anions formed :  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{OH}^-$

(i) greater ~~the~~ reduction potential having cation reduces first.

$\therefore$  R.P. order.  $\text{Na}^+ < \text{H}^+ < \text{Cu}^{2+}$

$\therefore \text{Cu}^{2+}$  reduces at cathode and deposited at cathode as Cu.

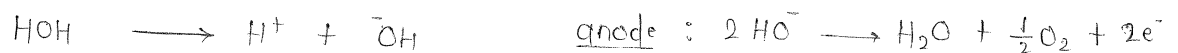
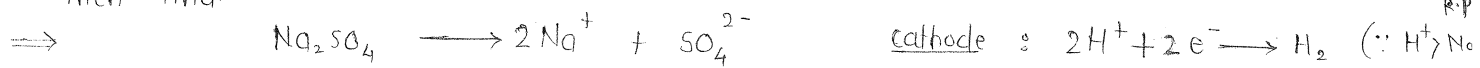
(ii) greater oxid<sup>n</sup> potential having anion oxidizes first.

$\therefore$  O.P. order :  $\text{Cl}^- > \text{OH}^- > \text{SO}_4^{2-}$

$\therefore \text{Cl}_2$  gas is liberated at anode.

Que-9 A current of 10 Amp. is passed through aq.  $\text{Na}_2\text{SO}_4$  for 965 sec.

then find.



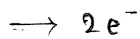
(i) quantity of electricity passed in C.

$$\Rightarrow Q = It = 10 \times 965 = 9650 \text{ C}$$

(ii) quantity of electricity passed in F

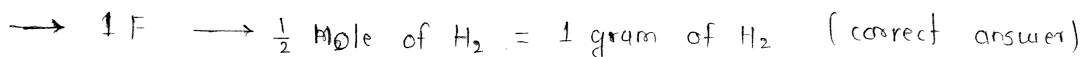
$$\Rightarrow \text{number of moles of electron involved in reaction} = 2F$$

(iii) No. of electrons involved in the electrode reaction.

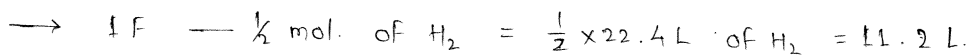


(iii) Amount of  $H_2$  liberated at cathode.

$$W = \frac{Q \times \text{Eq. wt}}{F} = \frac{9650 \times 1}{96500} = \frac{1}{10} = 0.1 \text{ gram (wrong answer)}$$



(iv) vol. of  $H_2$  liberated at STP

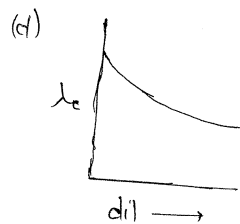
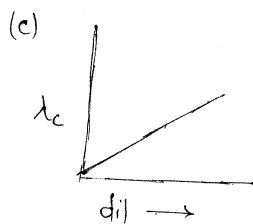
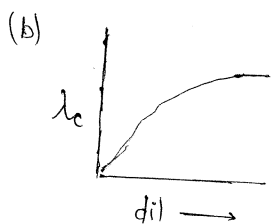
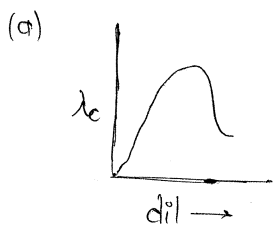


(v) Amount of  $O_2$  liberated at anode.

$\rightarrow$

### question based on conductance

Que-1 Which of the following represents plot between variation of equivalent conductance with dilution for a strong electrolyte.



$\Rightarrow$  for strong electrolyte, on dilution  $\lambda_c \uparrow$  slowly and reaches a maximum value and become constant & it is present by graph in option (ii)  
 $\therefore$  option (ii) is the correct answer.

Que-2 Specific conductance of decinormal solution of KCl is  $0.0112 \Omega^{-1} \text{ cm}^{-1}$ . The resistance of a cell containing the sol<sup>n</sup> was found to be  $56 \Omega$ . What is the cell constant.

$$\Rightarrow K = 0.0112 \Omega^{-1} \text{ cm}^{-1} \quad C_N = 0.1 N \quad R = 56 \Omega \quad x = ?$$

$$R = \rho \cdot \frac{l}{a} = \frac{1}{K} x \quad \Rightarrow \quad R = \frac{x}{K} \quad \Rightarrow \quad \boxed{x = R \cdot K}$$

$$x = 56 \times 0.0112 = 0.56 \times 1.12 \text{ cm}^{-1} = 0.6272 \text{ cm}^{-1}$$

### questions based on Kohlrausch's law

Que-1 The limiting  $\mu_{\infty}$  of NaCl, NaI & RbI are 12.7, 10.8, 9.1  $\text{mS} \cdot \text{m}^2 \cdot \text{mol}^{-1}$  respectively. The limiting  $\mu_{\infty}$  of RbCl would be

- (i) 32.6  $\text{mS} \cdot \text{m}^2 \cdot \text{mol}^{-1}$       (ii) 7.2      (iii) 14.4      (iv) 11.0.

$$\begin{aligned} \mu_{\infty}(\text{RbCl}) &= \mu_{\infty}(\text{NaCl}) + \mu_{\infty}(\text{RbI}) - \mu_{\infty}(\text{NaI}) \\ &= 12.7 + 9.1 - 10.8 = 21.8 - 10.8 \end{aligned}$$

$$\mu_{\infty}(\text{RbCl}) = 11.0 \text{ mS} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

$\therefore$  option (iv) is the correct answer.

Que-2 The  $\mu_{\infty} / \lambda_m^{\infty}$  for  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ , KCl, HCl &  $\text{HCOONa}$  at 298K are



same unit and at the same temp. is

(i) 381

(ii) 405

(iii) 429

(iv) 531.

$$\begin{aligned}\Rightarrow \lambda_m^\circ(\text{HCOOH}) &= \lambda_m^\circ(\text{HCOONa}) + \lambda_m^\circ(\text{HCl}) - \lambda_m^\circ(\text{NaCl}) \\ &= \lambda_m^\circ(\text{HCOONa}) + \lambda_m^\circ(\text{HCl}) - \left\{ \frac{1}{2} \lambda_m^\circ(\text{Na}_2\text{SO}_4) + \lambda_m^\circ(\text{KCl}) - \frac{1}{2} \lambda_m^\circ(\text{K}_2\text{SO}_4) \right\} \\ &= 105 + 426 - \left( \frac{1}{2} \times 260 + 150 - \frac{1}{2} \times 308 \right) = 631 - (130 + 150 - 154) \\ &= 631 - 126 = \underline{405} \text{ S. cm}^2 \cdot \text{mol}^{-1}\end{aligned}$$

$\therefore$  option (ii) is the correct answer.

Que-3 Kohlrausch's law is applicable for dilute solution of

(i) KCl in hexane

(ii) HCl in  $\text{H}_2\text{O}$

(iii)  $\text{CH}_3\text{COOH}$  in  $\text{H}_2\text{O}$

(iv)  $\text{C}_6\text{H}_5\text{COOH}$  in  $\text{C}_6\text{H}_6$ .

$\Rightarrow$  Kohlrausch's law is applicable to strong electrolytic solution. ( $\alpha = \text{maximum}$ )

$\therefore$  option (ii) is the correct answer.

$\uparrow$

Hint - Kohlrausch's law is applicable when electrolyte dissociates completely at  $\infty$  dilution.

Que-4 If conc. is increased to 4 times, its original value, the change in molar conductivity is ? (where  $b = \text{Kohlrausch constant}$ )

(i) 0

(ii)  $b\sqrt{2}$

(iii)  $2b\sqrt{c}$

(iv)  $4b\sqrt{c}$

$\Rightarrow$  A/c Kohlrausch law.

$$\lambda_m = \lambda_m^\circ - b\sqrt{c} \quad \text{--- (1) initial conc.}$$

$$\lambda'_m = \lambda_m^\circ - b\sqrt{4c} \quad \text{--- (2) 4 time increment in conc.}$$

$$= \lambda_m^\circ - 2b\sqrt{c} \quad \text{--- (2)}$$

$$\therefore \text{change} = \lambda_m - \lambda'_m = -b\sqrt{c} + 2b\sqrt{c} = \underline{b\sqrt{c}}$$

$\therefore$  option (ii) is the correct answer.

Que-5 Molar conductance of  $\text{M}^+$  &  $\text{A}^-$  are 70 & 60  $\text{S}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$  resp.

$K$  of saturated sol<sup>n</sup> of MA is  $= 1.3 \times 10^{-5} \text{S}^{-1} \cdot \text{cm}^{-1}$ . Solubility of MA = ?

(i) 0.1 mol/l.

(ii) 0.01 mol/litre

(iii) 0.001

(iv) 0.0001 mol/litre.

$$\Rightarrow \mu_+ = 70 \text{ S}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}, \quad \mu_- = 60 \text{ S}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}, \quad K = 1.3 \times 10^{-5} \text{ S}^{-1} \cdot \text{cm}^{-1} \quad S = ?$$

$$\mu_\infty = \mu_+ n_+ + \mu_- n_- = 70 \times 1 + 60 \times 1 = \underline{130} \text{ S}^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$$

$$S = \frac{1000 K}{c} = \frac{10^3 \times 1.3 \times 10^{-5}}{1 \times 10^2} = 10^{-2} \times 10^{-2} = 10^{-4} \text{ mol/L} = 0.0001 \text{ M.}$$

∴ option (v) is the correct answer.

**Que-6** The specific conductance of saturated solution of AgCl is found to  $1.86 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$  and that of  $\text{H}_2\text{O}$  is  $6 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ . The solubility of AgCl is

given  $\lambda_{\text{AgCl}}^{\circ} = 137.2 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$

$\begin{aligned} \rightarrow K_{\text{solution}} &= 1.86 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1} \\ K_{\text{H}_2\text{O}} &= 6 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1} \\ \lambda_{\text{AgCl}}^{\circ} &= 137.2 \Omega^{-1} \text{ cm}^2 \text{ eq}^{-1} \\ S_{\text{AgCl}} &= ? \end{aligned}$	$\begin{aligned} K_{\text{AgCl}} &= K_{\text{soln}} - K_{\text{H}_2\text{O}} \\ &= 1.86 \times 10^{-6} - 6 \times 10^{-8} \\ &= (1.86 - 0.06) \times 10^{-6} \\ &= 1.80 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1} \end{aligned}$	$\begin{aligned} S_{\text{AgCl}} &= \frac{10^3 K_{\text{AgCl}}}{\lambda_{\text{AgCl}}^{\circ}} = \frac{10^3 \times 1.80 \times 10^{-6}}{137.2} \\ &= \frac{1.80 \times 10^{-3}}{137.2} = \frac{1.800}{1372} \times 10^{-5} \\ S_{\text{AgCl}} &= 1.3 \times 10^{-5} \text{ M} \end{aligned}$
---	---	--

**Que-7** For strong electrolyte, the value of molar conductivity at  $\infty$  dilution are given below. calculate  $\lambda_m^{\infty}$  of  $\text{Ba}(\text{OH})_2$

$$\lambda_m^{\infty}(\text{BaCl}_2) = 280 \times 10^{-4}, \quad \lambda_m^{\infty}(\text{NaCl}) = 126.5 \times 10^{-4}, \quad \lambda_m^{\infty}(\text{NaOH}) = 248 \times 10^{-4}$$

$$\begin{aligned} \Rightarrow \lambda_m^{\infty}[\text{Ba}(\text{OH})_2] &= \lambda_m^{\infty}(\text{BaCl}_2) + 2 \times \lambda_m^{\infty}(\text{NaOH}) - 2 \times \lambda_m^{\infty}(\text{NaCl}) \\ &= 280 \times 10^{-4} + 2 \times 248 \times 10^{-4} - 2 \times 126.5 \times 10^{-4} \\ &= (280 + 496 - 253) \times 10^{-4} \\ &= 523 \times 10^{-4} \text{ S m}^2 \text{ mol}^{-1} \end{aligned}$$

**Que-8** Limiting ionic conductance of  $\text{A}^+$  &  $\text{B}^-$  are 80 & 60  $\Omega^{-1} \text{ cm}^2 \text{ gm. eq}^{-1}$ . determine transport no. of  $\text{A}^+$  and  $\text{B}^-$

$$\begin{aligned} \Rightarrow \lambda(\text{AB}) &= \lambda_+ + \lambda_- = 80 + 60 = 140 \Omega^{-1} \text{ cm}^2 \text{ gm. eq}^{-1} \\ t_+ &= \frac{80}{140} = \frac{4}{7} = 0.571 \quad t_- = \frac{60}{140} = \frac{3}{7} = 0.429 \end{aligned}$$

**Que-9** Eq. conductance at  $\infty$  dilution of  $\text{CH}_3\text{COOK}$ ,  $\text{H}_2\text{SO}_4$  &  $\text{K}_2\text{SO}_4$  are 120, 360, 180  $\Omega^{-1} \text{ cm}^2 \text{ gm. eq}^{-1}$  respectively. Determine  $\lambda_{\infty}$  of  $\text{CH}_3\text{COOH}$ .

$$\begin{aligned} \Rightarrow \lambda_{\infty}(\text{CH}_3\text{COOH}) &= \lambda_{\infty}(\text{CH}_3\text{COOK}) + \lambda_{\infty}(\text{H}_2\text{SO}_4) - \lambda_{\infty}(\text{K}_2\text{SO}_4) \\ &= 120 + 360 - 180 = 300 \Omega^{-1} \text{ cm}^2 \text{ gm. eq}^{-1} \\ \lambda_{\infty}(\text{CH}_3\text{COOH}) &= \lambda_{\infty}(\text{CH}_3\text{COOH}) \times Z \quad (Z = \text{charge} = 1) \\ &= 300 \times 1 = 300 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

**Que-10**  $\lambda_{\infty}$  of AB, CD and AD are 120, 360 & 180  $\Omega^{-1} \text{ cm}^2 \text{ gm. eq}^{-1}$  respectively. specific conductance of decinormal BC solution is  $3 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$ . determine % of dissociation of BC.

$$\begin{aligned} \Rightarrow \lambda_{\infty}(\text{BC}) &= \lambda_{\infty}(\text{AB}) + \lambda_{\infty}(\text{CD}) - \lambda_{\infty}(\text{AD}) = 120 + 360 - 180 = 300 \Omega^{-1} \text{ cm}^2 \text{ gm. eq}^{-1} \\ \lambda_c &= \frac{1000 \times K}{c} = \frac{10^3 \times 3 \times 10^{-4}}{10^{-1}} = 3 \times 10^1 = 3 \Omega^{-1} \text{ cm}^2 \text{ gm. eq}^{-1} \end{aligned}$$

$$\alpha = \frac{100}{100} = \frac{100}{100} = 1.00 = 100\%$$

∴ dissociation of BC is 100%.

Que-11 Molar ionic conductivities of a ~~trivalent~~ bi-bivalent electrolytes are 50 + 80 S cm<sup>2</sup> mol<sup>-1</sup>. The molar conductance of the solution will be.

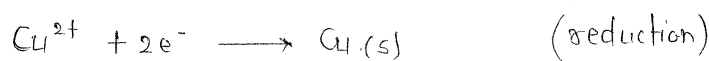
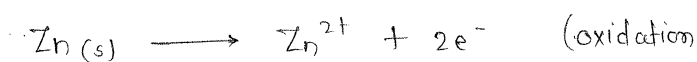
- (i) 260 S cm<sup>2</sup> mol<sup>-1</sup>      (ii) 130      (iii) 65      (iv) 520.

⇒ bi-bivalent electrolyte → A<sup>2+</sup> + B<sup>2-</sup>      Ex.: ~~K<sub>2</sub>SO<sub>4</sub>~~ MgSO<sub>4</sub>.

$$\mu_{\text{soln}} = n_+ \cdot \mu_+ + n_- \cdot \mu_- = 1 \times 50 + 1 \times 80 = \underline{130 \text{ S cm}^2 \text{ gm. eq}^{-1}}$$

### Questions based on Nernst Equation.

Que-1 The correct ΔG for the cell reaction, involving steps, is



(i)  $\Delta G^\circ + \frac{RT}{nF} \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$       (ii)  $\Delta G^\circ + RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$

(iii)  $\Delta G^\circ - RT \ln \frac{a_{\text{Zn}}}{a_{\text{Cu}^{2+}}}$       (iv)  $\Delta G^\circ - RT \ln \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}}$

⇒  $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln K. \implies \Delta G = \Delta G^\circ_{\text{cell}} + RT \ln K.$

$$\therefore \Delta G = \Delta G^\circ + RT \ln \left( \frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right)$$

∴ option (ii) is the correct answer.

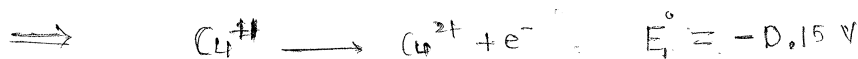
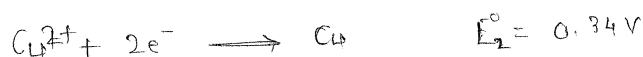
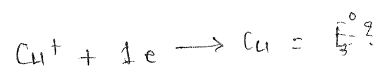
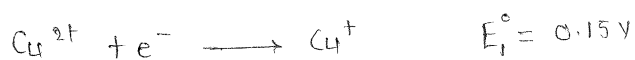
Que-2 The temperature dependence of electrochemical cell potential is

- (i)  $\frac{\Delta G}{nFT}$       (ii)  $\frac{\Delta H}{nF}$       (iii)  $\frac{\Delta S}{nF}$       (iv)  $\frac{\Delta S}{nFT}$

⇒ A/c thermodynamic relationship, temperature coefficient is given by

$$\left( \frac{\partial E_{\text{cell}}}{\partial T} \right)_P = \frac{\Delta S}{nF} \implies \text{option (iii)} \text{ is the correct answer}$$

Que-3 If for the half cell reaction, Calculate E° for



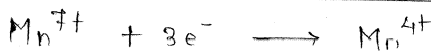
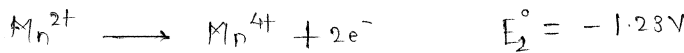
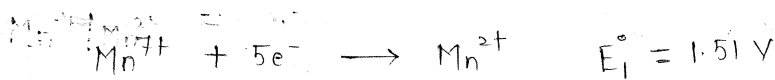
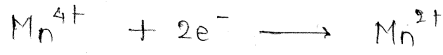
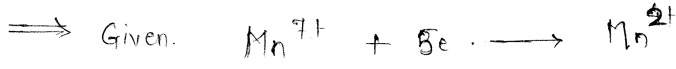
$$E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3} = \frac{1 \times (-0.15) + 1 \times 0.34}{2} = 0.095 \text{ V}$$

$$E_3^\circ = \frac{1 \times (-0.15) + 2 \times 0.34}{1} = -0.15 + 0.68 = +0.53 \text{ V}$$

$$\therefore \boxed{E_3^\circ = +0.53 \text{ V}}$$

Que-4 Given  $E_{\text{Mn}^{7+}|\text{Mn}^{2+}}^\circ$  &  $E_{\text{Mn}^{4+}|\text{Mn}^{2+}}^\circ$  are 1.51 V and 1.23 V. Calculate

$$E_{\text{Mn}^{7+}|\text{Mn}^{4+}}^\circ = ?$$



$$\therefore E_3^\circ = \frac{n_1 E_1^\circ + n_2 E_2^\circ}{n_3}$$

$$= \frac{5 \times 1.51 + 2 \times (-1.23)}{3}$$

$$= \frac{7.55 - 2.46}{3}$$

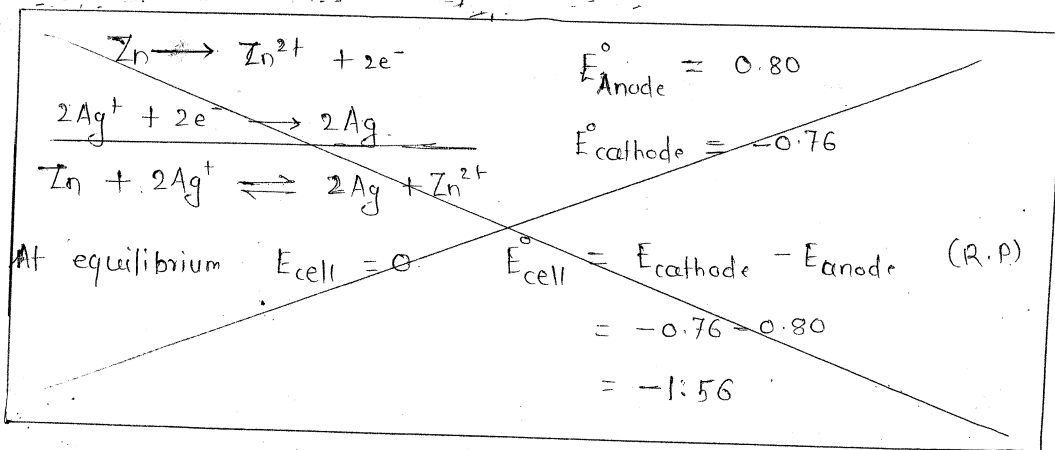
$$= \frac{5.01}{3} = 1.67 \text{ V}$$

$$\boxed{E^\circ = 1.67 \text{ V}}$$

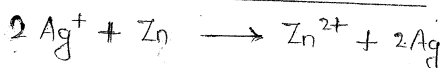
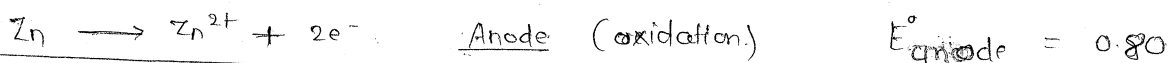
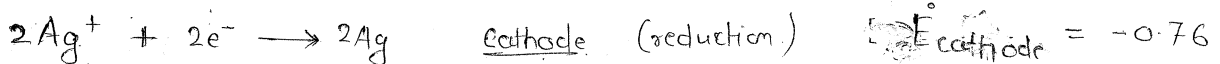
$$\therefore \boxed{E_{\text{Mn}^{7+}|\text{Mn}^{4+}}^\circ = 1.67 \text{ V}}$$

Que-5 Standard reduction potential of Ag & Zn are 0.80 & -0.76 V respectively.

Calculate equilibrium constant for the cell reaction of  $\text{Zn} + 2\text{Ag}^+ \rightleftharpoons \text{Zn}^{2+} + 2\text{Ag}$ .



$$\text{R.P.}(\text{Ag}^+) > \text{R.P.}(\text{Zn}^{2+})$$



At equilibrium  $E_{\text{cell}} = 0$ ,  $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (\text{R.P.})$

$$= -0.76 - 0.80$$

$$= -1.56$$

$$\log K = -52$$

$$\therefore \boxed{K = 10^{-52}}$$

$$\frac{0.059}{n} \log K = E_{\text{cell}}^\circ$$

$$\therefore \log K = \frac{n E_{\text{cell}}^\circ}{0.059} = \frac{2 \times (-1.56)}{0.059} = \frac{-1.56}{0.03} = \frac{-1.56}{0.03} = -52$$

Que-1 : Calculate  $E_J$  at  $25^\circ\text{C}$  between two solutions of HCl having mean ionic activities of 0.01 & 0.001,  $t_+$  in HCl will be taken as 0.83.

$$\Rightarrow a_1 = 0.01, \quad a_2 = 0.001, \quad t_+ = 0.83, \quad \therefore t_- = 0.17$$

Given that electrode is reverse to cation.

$$\begin{aligned} \therefore E_J &= (t_- - t_+) \frac{0.059}{n} \log \left( \frac{a_2}{a_1} \right) \\ &= (0.17 - 0.83) \times \frac{0.059}{1} \log \left( \frac{0.001}{0.01} \right) \\ &= -0.66 \times 0.06 \times \log \left( \frac{1}{10} \right) \\ &= -0.66 \times 8 \times 10^{-2} \times \log 10^{-1} \\ &= +2 \times 1.98 \times 10^{-2} \times \log 10 \\ &= 2 \times 1.98 \times 10^{-2} \text{ V} = 3.96 \times 10^{-2} \text{ V} = \underline{\underline{0.0396 \text{ V}}} \end{aligned}$$

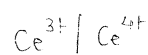
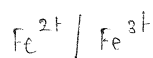
Que-2  $\text{C}_4\text{H}_{10} + \frac{13}{2} \text{O}_2 (\text{g}) \longrightarrow 4 \text{CO}_2 (\text{g}) + 5 \text{H}_2\text{O} (\text{l})$ , if the change in Gibbs free energy of this reaction is 2746.06 kJ/mol, involving  $26e^-$ , its open circuit voltage is

- (i) 1.55 V      (ii) 1.09 V      (iii) 3.15 V      (iv) 2.06 V

$$\begin{aligned} \Rightarrow n &= 26, \quad -\Delta G = 2746.06 \text{ kJ/mol} \quad E_{\text{cell}} = ? \\ &= 2746.06 \times 10^3 \text{ J/mol} \\ -\Delta G &= nFE_{\text{cell}} \quad \therefore E_{\text{cell}} = \frac{-\Delta G}{nF} = \frac{2746.06 \times 10^3}{26 \times 96500} = \frac{105066}{96500} = \frac{1050}{965} \\ &= 1.088 \text{ V} \\ &\approx \underline{\underline{1.09 \text{ V}}} \end{aligned}$$

### # Redox titration #

Solution contains same species in two different oxidation state — redox electrode



Redox titration      Ferrous ammonium sulphate vs ~~ferrous~~ Ceric ammonium sulphate.



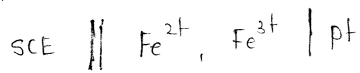
beaker

~~pipette~~ Burette

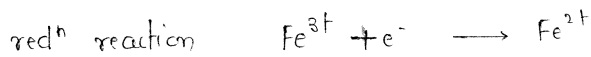
→ Reference electrode

$$\text{SCE R.P.} = 0.242 \text{ eV}$$

→ Cell representation

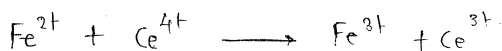


→ cell potential

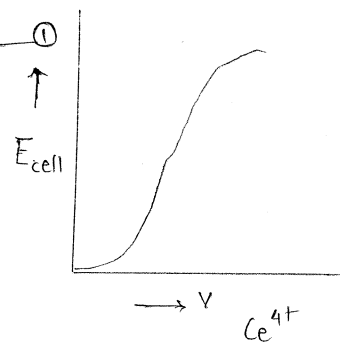


$$\begin{aligned} E_{\text{Fe}^{3+}/\text{Fe}^{2+}} &= E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.059 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \\ &= E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \end{aligned}$$

$$\therefore E_{\text{cell}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + 0.059 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} - E_{\text{SCE}} (0.242) \quad \text{--- ①}$$



On adding Cerria ammonium sulphate  $E_{\text{cell}} \uparrow$



→ At half-neutralization point.

$$[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$$

$$E_{\text{cell}} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.242 \quad \longrightarrow \text{from equation ①}$$

$$E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = E_{\text{cell}} (\text{Half neutralization point}) + 0.242$$

↙ calculated from graph.

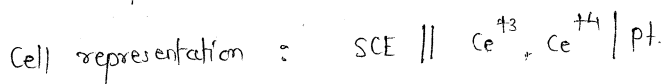
→ After the complete assumption of  $\text{Fe}^{2+}$

→ before equivalence point  $E_{\text{cell}}$  is controlled by

$$\frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \text{ ratio}$$

→ After equivalence point, the  $E_{\text{cell}}$  can be controlled by

$$\frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \text{ because } [\text{Fe}^{2+}] \text{ becomes zero.}$$



$$E_{\text{cell}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - 0.059 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} - 0.242$$

$$E_{\text{cell}} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} + 0.059 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} - 0.242 \quad \text{--- ②}$$

→ After equilibrium  
 $\frac{[Ce^{4+}]}{[Ce^{3+}]}$  ratio.

→ At equivalence point

$$eq^n 1 = eq^n 2$$

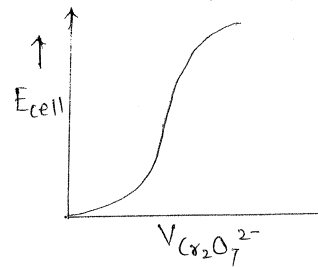
$$n \text{ (1)} + eq^n \text{ (2)} \quad 2E_{cell} = E_{Fe^{3+}/Fe^{2+}}^{\circ} + E_{Ce^{4+}/Ce^{3+}}^{\circ} - 2 \times 0.242 - 0.059 \log \frac{[Fe^{2+}][Ce^{4+}]}{[Fe^{3+}][Ce^{3+}]}$$



$$2E_{cell} = E_{Fe^{3+}/Fe^{2+}}^{\circ} + E_{Ce^{4+}/Ce^{3+}}^{\circ} - 0.242 \times 2$$

$$\therefore E_{cell} = \frac{E_{Fe^{3+}/Fe^{2+}}^{\circ} + E_{Ce^{4+}/Ce^{3+}}^{\circ}}{2} - 0.242$$

Example @  $Fe^{2+}$  Vs  $K_2Cr_2O_7$  ( $Cr^{6+}$ )  
 ↑ beaker ↑ burette.



→ Acidic condition.



$$E_{cell} = \frac{E_{Fe^{3+}/Fe^{2+}}^{\circ} + E_{Cr^{6+}/Cr^{3+}}^{\circ}}{2} - 0.242$$

### # Conductometric titration #

principles : Conductance is directly depends on

i) number of ion.

ii) mobility of ion / speed of ions.

End point : conductivity values

⇓

conductivity meter

Advantages : (i) No indicator required

(ii) applicable to coloured sol<sup>n</sup> also

(iii) W.A/W.B. titration easily done.

(iv) more accurate & precise result are obtained.







v) strong acid Vs weak base : HCl vs  $\text{NH}_4\text{OH}$

→ Upto completion.

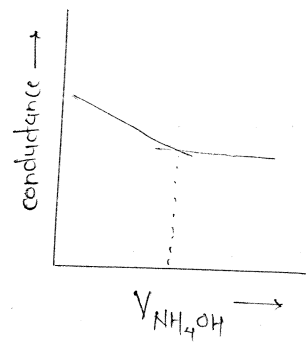
No. of  $\text{H}^+$  ions ↓ es, conductance decreases ↓ es sharply upto complete consumption of HCl.

→ After completion.

$\text{NH}_4\text{OH}$  remains undissociated

↳ no. of ion become steady

↳ hence conductance also become steady.



vii) mixture of acids Vs weak base :  $(\text{HCl} + \text{CH}_3\text{COOH})$  Vs  $\text{NH}_4\text{OH}$

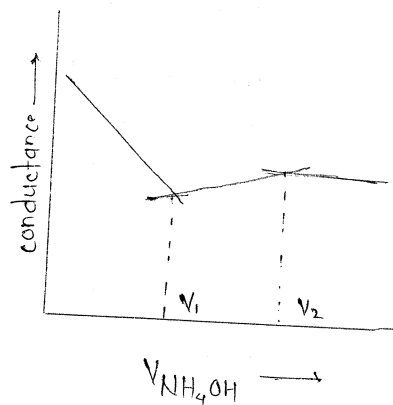
→ Upto complete consumption of HCl, conc. of

$\text{H}^+$  ion decreases ↓ es, ∴ conductance also ↓ es sharply.

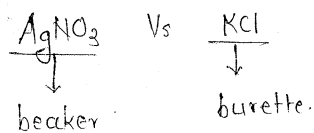
→ Upto complete consumption  $\text{CH}_3\text{COOH}$ , no. of  $\text{CH}_3\text{COO}^- \text{NH}_4^+$  ions increases, ∴ conductance also increase ↑ es slowly.

→ After completion. or complete consumption of  $\text{CH}_3\text{COOH}$  & HCl.

No. of  $\text{NH}_4\text{OH}$  remains unchanged ∴ conductance become steady.



# Precipitation titration #



conductance :  $\text{Ag}^+ \approx \text{K}^+$

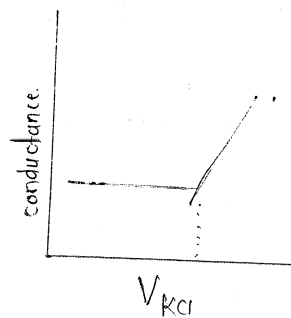
→ After complete consumption of  $\text{AgNO}_3$

no. of  $\text{K}^+$  &  $\text{Cl}^-$  ↑ es

conductance ↑

→ Upto complete consumption of  $\text{AgNO}_3$

conductance :  $\text{Ag}^+ \approx \text{K}^+$  conductance remain constant



## # IONIC STRENGTH (I) #

→ Electrolyte solution : ion-ion interaction occurs / takes place

↓  
results in deviation from ideal behaviour.

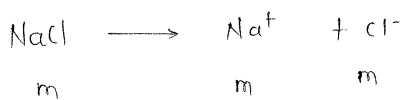
→ It is measure of electrical intensity / strength of electric field present in solution

$$I = \frac{1}{2} \sum_i C_i Z_i^2$$

$C_i$  - concentration of ion

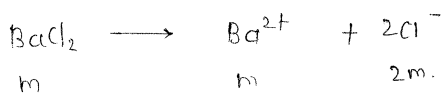
$Z_i$  - charge number on ion.

(i) 1:1 Electrolyte = NaCl, KCl →  $I = ?$



$$I = \frac{1}{2} (m \times 1^2 + m \times 1^2) = \frac{1}{2} (2m) = m.$$

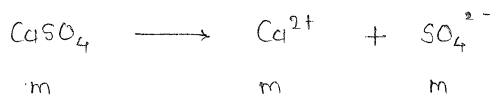
(ii) 1:2 electrolyte = BaCl<sub>2</sub>, CaCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub> or 2:1 electrolyte.



$$I = \frac{1}{2} (m \times 2^2 + 2m \times 1^2) = \frac{1}{2} (4m + 2m)$$

$$I = \frac{1}{2} \times 6m = 3m$$

(iii) 2:2 electrolyte = CaSO<sub>4</sub>, MgSO<sub>4</sub>



$$I = \frac{1}{2} (m \times (2)^2 + m \times (-2)^2) = \frac{1}{2} (4m + 4m) = \frac{1}{2} \times 8m$$

$$I = 4m$$

Note

$$\left. \begin{array}{l} 1:1 \text{ electrolyte} \\ 2:1 / 1:2 \text{ electrolyte} \\ 2:2 \text{ electrolyte} \end{array} \right\} \begin{array}{l} I = m \\ I = 3m \\ I = 4m \end{array} \quad \left. \begin{array}{l} \\ \\ \\ \end{array} \right\} m = \text{molar conc. / simply conc.}$$

## # Debye-Huckel Theory of Strong electrolytes #

assumption (i) strong electrolyte undergo 100% dissociation or complete ionization at all concentration.

(ii) With dilution, no change in number of ion but speed of ions ↑ es

∴ conductivity also ↑.

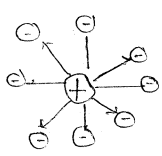
(iii) At high conc., ~~inter~~ interionic interaction is present, so speed/mobility of ion is low, conductivity is also low.

(iv) With dilution, attractive interionic interaction get reduced, so mobility of ion increases, conductivity is also increases.

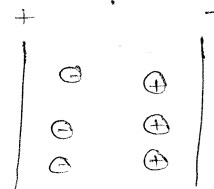
(vi) At high conc. two interaction operates

- 1) Asymmetric effect / Relaxation effect
- 2) Electrophoretic effect.

1) Asymmetric Effect. - ion-ion interaction.



→ In absence of electric field, symmetric ionic atmosphere is present.



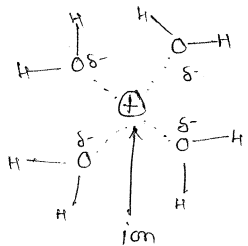
asymmetric ionic atmosphere

-ve charge ion → Under influence of electric field, asymmetric ionic atmosphere is present

+ve charge ion

→ Then mobility of ion decreases due to formation of asymmetric ionic atmosphere.

2) Electrophoretic effect. - ions-solvent interaction



→ On applying electric field, central ion moves against the solvent molecules

→ So mobility of central ion decreases and the conductivity also ↓es.

→ Deviation from ideal behaviour of electrolyte

(i) Electrostatic forces between ions is given by.

A/c Coulomb's law

$$F \propto \frac{Q_1 Q_2}{r^2}$$

$Q_1$  &  $Q_2$  - charges on oppositely charged ion

$r$  - distance between ions

$$F = \frac{1}{D} \frac{Q_1 Q_2}{r^2}$$

$D$  - dielectric constant

Dielectric constant : measure of weakening of attractive forces between ions.

$D \uparrow$  weakening of attractive forces  $\uparrow$ es

(vii) Ions are assumed as uniformly charged spheres.

(viii) Difference b/w size of ions is not considered.

(ix) In case of weak electrolyte

$$d = \frac{\lambda_c}{\lambda_{\infty}}$$

but for strong electrolyte  $d$  can not be calculate.

→ Due to ion-ion attractive interaction, the chemical potential decreases

$$u_i^{IS} = u_i^{\circ} + RT \ln \alpha_i = u_i^{\circ} + RT \ln m_i$$

$$u_i^{NIS} = u_i^{\circ} + RT \ln a_i$$

$u_i$  - chemical potential.

IS - ideal solution

$a_i$  - activity

NIS - nonideal solution.

$m$  = molar conc.

∴ decrease in chemical potential / energy.

$$\Delta u = u_i^{NIS} - u_i^{IS}$$

$$\Delta u = RT \ln \left( \frac{a_i}{m_i} \right)$$

$$\Delta u = RT \ln (\gamma_{\pm})$$

$(\gamma_{\pm})$  - indicates decrease in chemical potential due to ion-ion interaction

$$\therefore (a_i = \gamma_{\pm} m)$$

→ Based on these assumptions Debye-Huckel gives relation between  $\lambda_m$  and conc.

# Debye-Huckel-Onsager Equation #

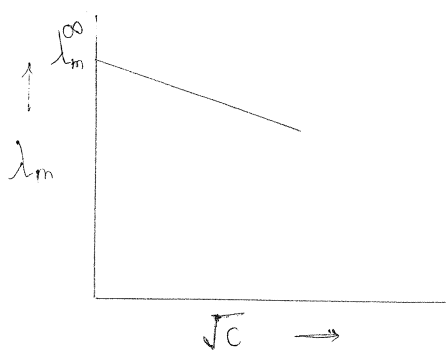
$$\lambda_m = \lambda_m^{\infty} - (A + B \lambda_m^{\infty}) \sqrt{c} \quad \text{--- ①}$$

$$A = \text{Electrophoretic effect} = \frac{82.4}{(DT)^{3/2} \eta}$$

$$B = \text{Relaxation effect} = \frac{0.2 \times 10^5}{(DT)^{3/2}}$$

$D$ : dielectric constant.

$\eta$ : viscosity.



→ validity of D-H-O equation:

(i) From  $c \rightarrow 0 \Rightarrow \lambda_m \rightarrow \lambda_m^{\infty}$

(ii) It gives exact result for 1:1 electrolyte upto  $C = 2 \times 10^{-2} M$ .

(iii) For higher valence electrolyte (2:1, 2:2, 1:2) upto  $C = 4 \times 10^{-5} M$ .

(iv) gives good results for electrolytes in non-aqueous solvent.

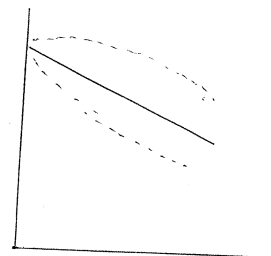
Ex : methanol.

→ Limitations of D.H.O. equation.

(i) application/applicable to dilute solutions only.

(ii) Conductivity value we are getting theoretically by Debye-Huckel-Onsager equation are less than experimental values.

(iii). Conductivity values obtained by D.H.O. equation are higher than experimental values.



# Debye-Huckel limiting law #  $\gamma_{\pm} \propto \sqrt{I}$

→ gives relation b/w mean ionic activity coefficient ( $\gamma_{\pm}$ ) and ionic strength ( $I$ )

$\gamma_{\pm}$  : indicates deviation from ideal behaviour due to ion-ion interactions.

$$\rightarrow \Delta G = RT \ln(\gamma_{\pm})$$

$\gamma_{\pm}$  : indicates decrease in chemical potential due to ion-ion interactions.

→ provide theoretical method to calculate deviation from ideal behaviour.

$$\boxed{\log \gamma_{\pm} = -A Z_+ Z_- \sqrt{I}}$$

A - constant depend on solvent & temperature

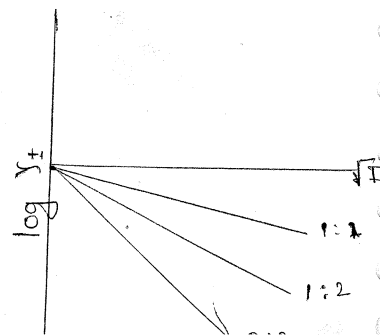
For  $H_2O$  at  $25^\circ C$   $A = 0.509$

∴ For water used as solvent.

$$\boxed{\log \gamma_{\pm} = -0.509 Z_+ Z_- \sqrt{I}}$$

) For 1:1 electrolyte  $Z_+ = 1$   $Z_- = 1$

$$\text{slope, } m = -0.509 (1)(1) = -0.509$$



slope  $m = -0.509 \times 1 \times 2 = -2 \times 0.509 = -1.018$

$$\log \gamma_{\pm} = \underbrace{-0.509}_{m} \underbrace{z_+ z_-}_{x} \sqrt{I}$$

(i) For 1:1 electrolyte.  $z_+ = 1, z_- = 1$ .

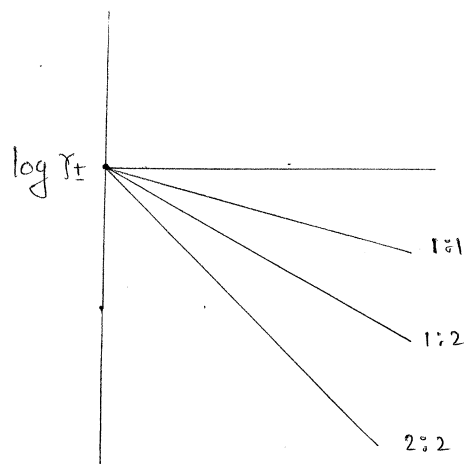
$$m = -0.509 \times 1 \times 1 = -0.509$$

(ii) For 1:2/2:1 electrolyte  $z_+ = 1, z_- = 2$

$$m = -0.509 \times 1 \times 2 = -0.509 \times 2$$

(iii) For 2:2 electrolyte  $z_+ = 2, z_- = 2$

$$m = -0.509 \times 2 \times 2 = -0.509 \times 4$$



→ conclusion from Debye-Huckel limiting law.

(i)  $\log \gamma_{\pm} = -ve$        $\gamma_{\pm} < 1$       -ve deviation.

(ii)  $c \rightarrow 0 \Rightarrow I = 0 \Rightarrow \log \gamma_{\pm} = 0 \Rightarrow \boxed{\gamma_{\pm} = 1}$

indicates no deviation from ideal behaviour.

(iii)  $\log \gamma_{\pm} = -0.509 z_+ z_- \sqrt{I}$

$\gamma_{\pm}$  ↓ due to ion-ion attractive interaction.

↓ in  $\gamma_{\pm}$  is more when charges on ions is high.

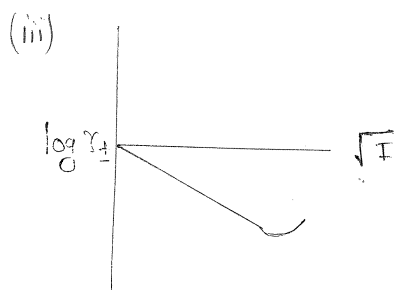
↓ in  $\gamma_{\pm}$  is more then I is high.

(iv) Dielectric constant D is low  $\Rightarrow$  ↓ in  $\gamma_{\pm}$  is more.

→ Limitation of DHLL

(i) It is applicable to dilute solution only.

(ii) For two different 1:1 electrolyte or for all 1:1 electrolyte same graph is obtained but experimentally we get two different graphs for two different 1:1 electrolyte.



$\gamma_{\pm}$  start rising after reaching a minimum value and then increase is not explained by Debye Huckel's law.

## # Extended Debye-Huckel Limiting Law #

→ applied to higher conc. electrolyte solution.

→ two new terms are introduced.

(i)  $a$  - ion size parameter

(ii)  $B$  - temp & solvent parameter.

→

$$\log \gamma_{\pm} = \frac{-AZ_+Z_-\sqrt{I}}{1 + aB\sqrt{I}}$$

$$\log \gamma_{\pm} = (-AZ_+Z_-\sqrt{I}) (1 + aB\sqrt{I})^{-1}$$

$$\therefore (1+x)^{-1} = 1 - x + x^2 - x^3 + \dots$$

on neglecting higher order coefficient

$$(1+x)^{-1} = 1 - x.$$

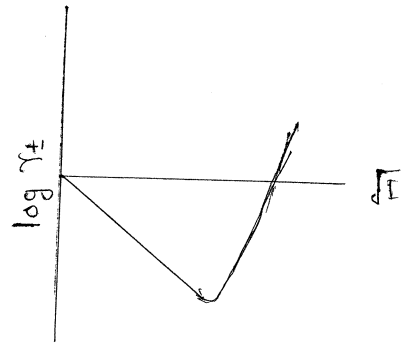
$$\log \gamma_{\pm} = (-AZ_+Z_-\sqrt{I}) (1 - aB\sqrt{I})$$

$$\log \gamma_{\pm} = -AZ_+Z_-\sqrt{I} + aABZ_+Z_-(\sqrt{I})^2$$

$$\boxed{\log \gamma_{\pm} = -AZ_+Z_-\sqrt{I} + aABZ_+Z_-\sqrt{I}}$$

At low  $I \Rightarrow \log \gamma_{\pm} = -ve \Rightarrow \gamma_{\pm} < 1$

At high  $I \Rightarrow \log \gamma_{\pm} = +ve \Rightarrow \gamma_{\pm} > 1$

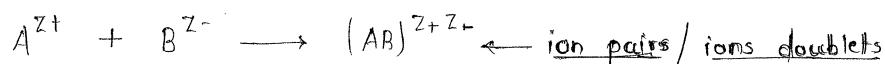


## # Bjerrum Theory of Ion association #

→ Debye-Huckel theory

calc. conductance  $\ll$  exp. conductance

→ Debye-Huckel theory doesn't consider ion pairs or ions doublets



number of ions  $\downarrow \Rightarrow$  conductance  $\downarrow$

→ Ion association occurs temporarily.

→ Electrolyte is ionized completely but not dissociated.

→ On dilution, ion pairs formation decreases, then we say that electrolyte is completely ionized and dissociated.

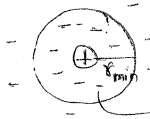
→ A/c to Bjerrum theory, ion pair formation takes place with potential energy  $\gg \frac{2kT}{r}$



→ distance,  $r$  where  $r > r_{\text{minimum}}$  value.

$$r_{\text{min.}} = \frac{Z_+ Z_- e^2}{2DkT}$$

ion pair not formed



ion pairs forms

$$r > r_{\text{min}}$$

no formation of ion pairs/ion doublet

hence Debye Huckel's theory holds good in such case.

→ Ions which are present within the sphere forms ion pairs. and ions present outside the sphere donot involved in ion pair formation

→ As  $r_{\text{min}}$  value increases, numbers of ions involves in ion pair formation is more. Therefore ~~more~~ no. of ion pairs increases.

→ As charges on ion is high  $\implies r_{\text{minimum}}$  is high. } ← probability for ion association is also high.  
 → Lower is the dielectric constant  $D \implies$  higher  $r_{\text{min.}}$  is  $r_{\text{min.}}$

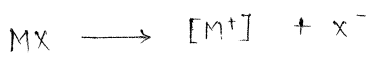
→  $r \leq r_{\text{min}}$  : ion pair/ion doublets formation occurs.

→ concept of ion association is based on conductivity measurement.

ion association  $\uparrow$  conductances  $\downarrow$ .

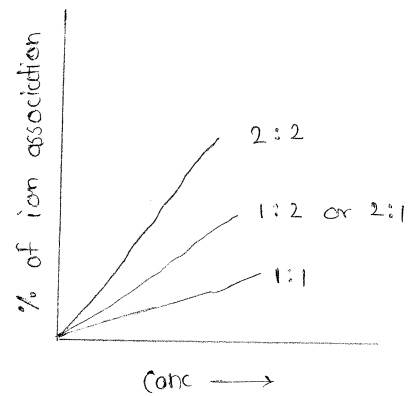
### # Ion association constant #

→ explains degree of association.



$$K_D = \frac{[M^+][X^-]}{[MX]}$$

$$K_A = \frac{1}{K_D} = \frac{[MX]}{[M^+][X^-]}$$



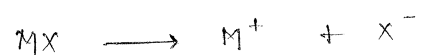
For non-ideal solution

$$K_A = \frac{a_{MX}}{a_{M^+} a_{X^-}} = \frac{\gamma_{MX} C_{MX}}{\gamma_{M^+} C_{M^+} \gamma_{X^-} C_{X^-}}$$



c                      c                      c                      conc.

let  $\theta$  = degree of ion association



$c\theta$                        $c(1-\theta)$                        $c(1-\theta)$

go                      go

$\theta = 10\%$

$$K_A = \frac{\gamma_{MX} \alpha \theta}{\gamma_{M^+} (1-\theta) \gamma_{X^-} c (1-\theta)}$$

For very dilute solution solution  $1-\theta \approx 1$ .  $\therefore \gamma_{MX} \rightarrow 1$

$$\therefore K_A = \frac{\gamma_{MX} \theta}{c} = \frac{\theta}{c}$$

$$\therefore \boxed{K_A = \frac{\theta}{c}}$$

$\theta$  :  $\theta$  of degree of ion association.

$c$  : conc.

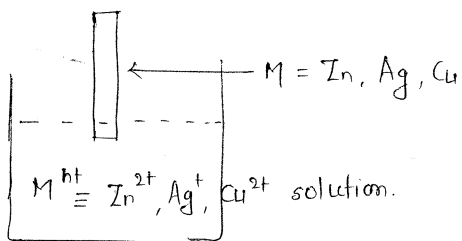
### # Debye-Huckel-Bjerrum Equation #

$$\log \gamma_{\pm} = \frac{-A \cdot z_+ z_- \sqrt{c(1-\theta)}}{1 + a q \sqrt{c(1-\theta)}}$$

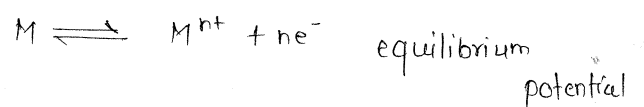
$q$  - closest distance between two ions.

$a$  - ionic size parameter.

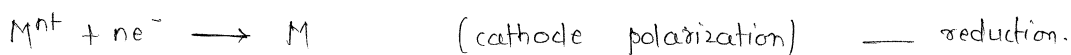
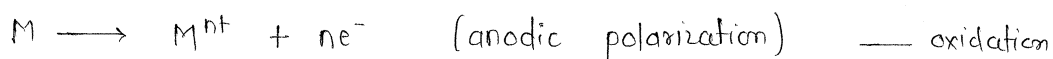
### # Electrode polarization # or # Concentration polarization #



$\rightarrow$  Equilibrium condition may be achieved after sometime.

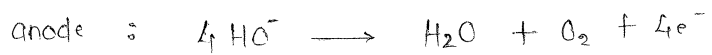
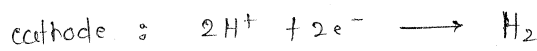
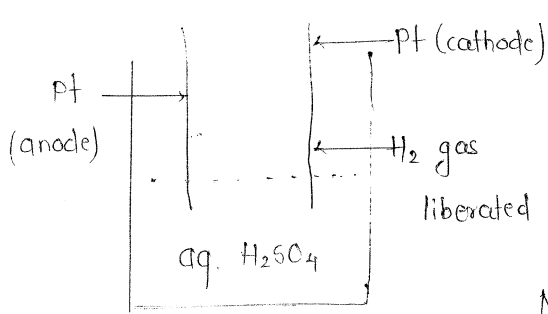


$\rightarrow$  On applying electrical voltage, equilibrium get disturbed and there is change in equilibrium potential value of an electrode by applying external voltage, the electrode is called polarizable electrode and phenomenon is called electrode polarization



$\rightarrow$  Electrode whose electrode equilibrium potential doesn't changes on applying external voltage, is called non-polarizable electrode Ex: SCE

$\rightarrow$  Change in electrode potential is due to change in conc. of ions near the electrode surface so it is called conc. polarization



Now Anode  $\rightarrow$  acts as  $\text{H}_2$  gas electrode. } Galvanic cell  
 Cathode  $\rightarrow$  acts as  $\text{H}_2$  gas electrode } formed  
 $\downarrow$   
 chemical E  $\rightarrow$  electrical emf

$\rightarrow$  Such emf produced is called back-emf or reverse emf and it is removed by continuous stirring or by increasing temp or by taking smooth electrode surface or by using oxidant.

### # Decomposition potential #

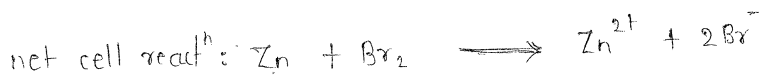
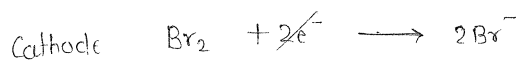
Reversible cell :-

$\rightarrow$  External voltage  $<$   $E_{\text{cell}}$  : causes no effect on cell reaction. i.e. chemical energy converted to electrical energy.

$\rightarrow$  External voltage  $=$   $E_{\text{cell}}$  : cell reaction stops. i.e. reaction reaches the equilibrium.

$\rightarrow$  External voltage  $>$   $E_{\text{cell}}$  : reverse reaction take place i.e. electrical energy convert to chemical energy. i.e. electrolysis takes place

Reversible cell :  $\text{Zn} | \text{Zn}^{2+} || \text{Br}^- | \text{Br}_2, \text{Pt}$ .



$$\text{Cell potential } E_{\text{cell}}^{\circ} = E_{\text{Br}_2 | \text{Br}^-}^{\circ} - E_{\text{Zn}^{2+} | \text{Zn}}^{\circ} \quad (\text{R.P.})$$

$$= 1.07 - (-0.76)$$

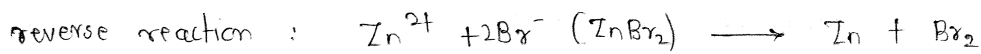
$$= 1.83 \text{ V}$$

if External voltage  $<$  1.83 V  $\rightarrow$  No effect on cell reaction

if External voltage  $=$  1.83 V  $\rightarrow$  cell reaction reaches the equilibrium

if external voltage  $\geq$  1.83 V  $\rightarrow$  reverse reaction takes place





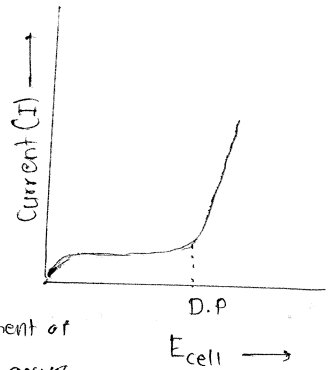
i.e. electrolysis of  $ZnBr_2$

→ The minimum potential required to start electrolysis process, is called as decomposition potential or discharge or deposition potential. The decomposition potential is obtained by the graph between current & cell potential.

→ Low potential → no current flow through solution.

potential (ext. voltage) increases → gradually → after reaching certain point, the flow of current takes place.

→ Decomposition potential is useful in qualitative analysis by using polarographic technique.

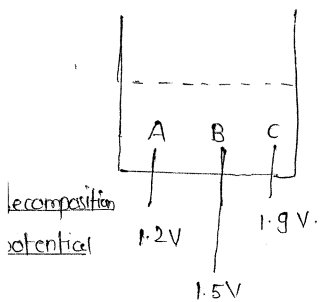


External potential = 0.1 ..... 1.2 V ..... 1.5 V

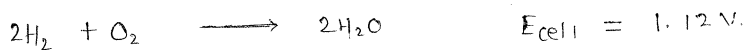
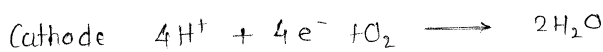
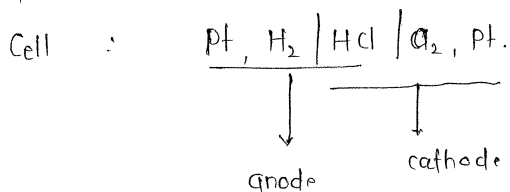
↓  
movement of A ions occurs

↓  
movement of B ions occurs

sudden rise in current is observe



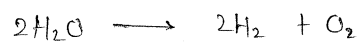
### # Over potential #



$E_{cell} = 1.12 V.$

if external potential < 1.12 V : No effect on cell reaction

if external potential > 1.12 V : reverse reaction takes place i.e. electrolysis of water takes place



But experimentally it is observed that 1.7 V is required to start electrolysis of water.

Excess voltage = Theoretical value - Exp. value

= 1.7 - 1.12

= 0.558 V ——— (over voltage)

→ excess voltage is required.

→ reduction of  $H^+$  ion is slow process. To enhance this rate, excess voltage is required.

→ deposition of  $H_2$  is slow process. To enhance the rate, excess voltage is required.

	Hydrogen	Oxygen
Theoretical value	1V	1.2V
Experimental value	1.3V	1.4V
$H_2$ over voltage	0.3V	0.2V ← $O_2$ Over voltage.

Que-1 Identify from the following the correct ionic strength for.

(i) 0.01 M NaCl solution.

(ii) 0.01 M  $Na_2SO_4$  solution.

- |     | (i)    | (ii)    |
|-----|--------|---------|
| (a) | 0.01 m | 0.01 m  |
| (b) | 0.01 m | 0.03 m  |
| (c) | 0.01 m | 0.025 m |
| (d) | 0.01 m | 0.015 m |

$\Rightarrow$  NaCl = 1:1 electrolyte  $I = C = 0.01$  m      Hence option (b) is the correct answer

$Na_2SO_4 = 1:2$  electrolyte  $I = 3C = 0.03$  m

Que 2 - Calculate the ionic strength of

(A) 0.15 m KCl solution

(B) 0.25 m  $K_2SO_4$  sol<sup>n</sup>

(C) ~~0.1~~ 0.2 m  $BaCl_2$  solution

∴ (D) a solution which is 0.1 m in KCl & 0.2 m in  $K_2SO_4$

→ A) KCl = 1:1 electrolyte  $\Rightarrow I = C = 0.15$  m.

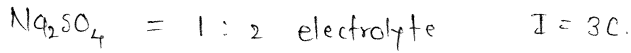
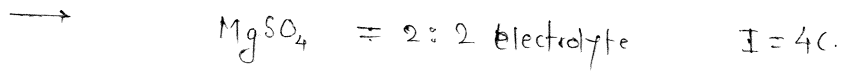
B)  $K_2SO_4 = 1:2$  electrolyte  $\Rightarrow I = 3C = 0.25 \times 3 = 0.75$  m

C)  $BaCl_2 = 2:1$  electrolyte  $\Rightarrow I = 3C = 0.2 \times 3 = 0.6$  m.

D)  $I = I_{KCl} + I_{K_2SO_4} = C + 3C = 0.1 + 3 \times 0.2 = 0.1 + 0.6 = 0.7$  m.

Que-3 The conc. of a  $MgSO_4$  solution having same ionic strength as that of 0.1 M  $Na_2SO_4$  solution is

- (i) 0.05 M      (ii) 0.067 M      (iii) 0.075 M      (iv) 0.133 M.



but

$$I_{MgSO_4} = I_{Na_2SO_4}$$

$$4C = 3C$$

∴ conc. of  $MgSO_4$  is 0.075 M.

$$4C = 3 \times 0.1$$

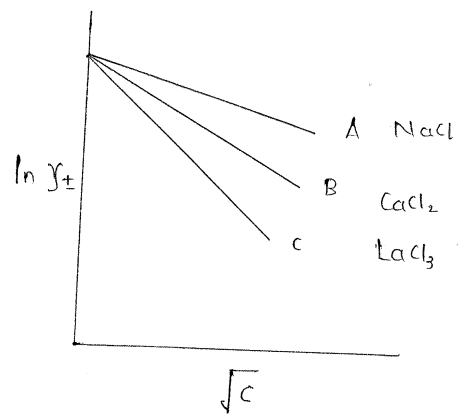
Hence option (iii) is the correct answer.

$$C = \frac{0.3}{4}$$

$$C = 0.075 M$$

Que-4 Aq. sol<sup>n</sup> of NaCl,  $CaCl_2$  &  $LaCl_3$  show the following plots of  $\ln \gamma_{\pm}$  Vs molar conc. C. The correct option is

	NaCl	$CaCl_2$	$LaCl_3$
1	C	B	A
2	A	B	C
3	A	C	B
C	C	A	B



→  $\ln \gamma_{\pm} = -AZ_+Z_-\sqrt{I}$

As charge increases  $\ln \gamma_{\pm}$  des.

∴ option (2) is the correct answer

Que-5 The ionic mobilities of  $NH_4^+$  and  $HCO_3^-$  are  $6 \times 10^{-4} \text{ v}^{-1} \text{ s}^{-1}$  and  $5 \times 10^{-4} \text{ v}^{-1} \text{ s}^{-1}$  resp. The transport numbers of  $NH_4^+$  &  $HCO_3^-$  respectively are

→  $t_{NH_4^+} = \xi$  &  $t_{HCO_3^-} = \xi$

(i) 0.545 & 0.455

(ii) 0.455 & 0.545

(iii) 0.090 & 0.910

(iv) 0.910 & 0.090

⇒  $t_{NH_4^+} = \frac{V_{NH_4^+}}{V_{NH_4^+} + V_{HCO_3^-}} = \frac{6 \times 10^{-4}}{6 \times 10^{-4} + 5 \times 10^{-4}} = \frac{6 \times 10^{-4}}{11 \times 10^{-4}} = \frac{6}{11} = 0.545$

$$\frac{V_{\text{HCO}^-}}{V_{\text{NH}_4^+} + V_{\text{HCO}^-}} = \frac{6 \times 10^{-4} + 5 \times 10^{-4}}{11 \times 10^{-4}} = \frac{11 \times 10^{-4}}{11 \times 10^{-4}} = 0.455$$

Que-7 The ionic strength of solution containing 0.008 M  $\text{AlCl}_3$  & 0.005 M  $\text{KCl}$  is

- (i) 0.134 M      (ii) 0.053 M      (iii) 0.106 M      (iv) 0.086 M

$\Rightarrow \text{AlCl}_3 = 3:1$  electrolyte       $\text{KCl} = 1:1$  electrolyte.

$$I = \frac{1}{2} (m \times 9 + 3m) = \frac{1}{2} \times 12m = 6m.$$

$$I = I_{\text{AlCl}_3} + I_{\text{KCl}}$$

$$= 6 \times 0.008 \text{ M} + 0.005 \text{ M} = 0.048 + 0.005 = 0.053 \text{ M}.$$

$\therefore$  option (ii) is the correct answer.

Que-8  $\theta$  is fraction of ions that get associated into ion pairs, at very large dilution the ion association constant  $K_A$  is given.

- (i)  $K_A = \theta \cdot c$       (ii)  $K_A = \frac{1}{\theta \cdot c}$       (iii)  $K_A = \frac{\theta}{c}$       (iv)  $K_A = \frac{c}{\theta}$

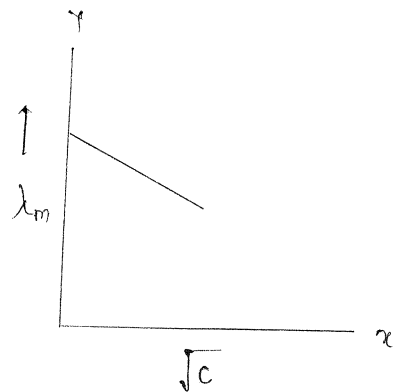
$\Rightarrow$  At large dilution

$$K_A = \frac{\theta}{c}$$

$\therefore$  option (iii) is the correct answer.

Que-9 A/c D.H.C equation a plot between  $\alpha$  and  $\gamma$  gives a straight line with -ve slope. with strong electrolyte  $\alpha$  &  $\gamma$  resp.

- |    |            |                    |
|----|------------|--------------------|
|    | $\alpha$   | $\gamma$           |
| 1) | $c$        | $\lambda_m$        |
| 2) | $\sqrt{c}$ | $\sqrt{\lambda_m}$ |
| 3) | $c$        | $\sqrt{\lambda_m}$ |
| 4) | $\sqrt{c}$ | $\lambda_m$        |



$\rightarrow$  D.H.C equation

$$\lambda_m = \lambda_m^{\infty} - (A + B\lambda_m^{\infty}) \sqrt{c}.$$

$$\alpha = \sqrt{c}$$

$$\gamma = \lambda_m$$

$\therefore$  option (iv) is the correct answer

Que-10 Three compounds A, B, C follow D.H. limiting law, the plot of  $\log \gamma_{\pm}$  Vs  $\sqrt{I}$  gave three straight line from

The slope of three straight line are in the ratio of 2:1:3, Then A, B, C are resp.

(i)  $\text{BaCl}_2$ ,  $\text{AlCl}_3$ ,  $\text{NaCl}$  (ii)  $\text{BaCl}_2$ ,  $\text{NaCl}$ ,  $\text{AlCl}_3$

(iii)  $\text{AlCl}_3$ ,  $\text{BaCl}_2$ ,  $\text{NaCl}$  (iv)  $\text{NaCl}$ ,  $\text{BaCl}_2$ ,  $\text{AlCl}_3$

$$\log \gamma_{\pm} = - \underbrace{0.509 Z_+ Z_-}_{m \text{ (slope)}} \sqrt{I}$$

2:1:3

A:B:C

$\text{BaCl}_2$  :  $\text{NaCl}$  :  $\text{AlCl}_3$

$\text{NaCl} : \text{BaCl}_2 : \text{AlCl}_3 = 1:2:2$

$\therefore$  option (ii) is the correct answer.

Que-11 What is value of  $\log \gamma_{\pm}$  for 0.01 m KCl solution.

(i) -0.509 (ii) +0.509 (iii) -0.0509 (iv) +0.059

$$\log \gamma_{\pm} = -0.509 Z_+ Z_- \sqrt{I}$$

$$= -0.509 \times 1 \times 1 \times \sqrt{0.01}$$

$\therefore$  KCl = 1:1 electrolyte.

$$= -0.509 \times \sqrt{10^{-2}}$$

$$= -0.509 \times 10^{-1} = -0.509 \times 0.1$$

$$= -0.0509$$

$\therefore$  option (iii) is the correct answer.

Que-12 A/c D.H. limiting law the conc. of a dilute aq. KCl soln is increased 4 times, the value  $\log \gamma_{\pm}$  will.

(i) decrease by a factor of 2

(ii) increase by a factor of 2

(iii) decrease by a factor of 4

(iv) increase by a factor of 4

$$\log \gamma_{\pm} = -0.509 Z_+ Z_- \sqrt{I}$$

$$\log \gamma_{\pm} = -0.509 Z_+ Z_- \sqrt{c}$$

$$\log \gamma_{\pm} = -0.509 Z_+ Z_- \sqrt{4c} = -0.509 Z_+ Z_- \times 2 \sqrt{c}$$



∴ option (1) is the correct answer.

Que-13 For a 2 M aq. NaCl solution, the  $\gamma_{\pm}$  & constant A are related as.

(i)  $\log \gamma_{\pm} = \sqrt{I} \times A$

(ii)  $\log \gamma_{\pm} = -\sqrt{I} \times A$

(iii)  $\log \gamma_{\pm} = 10^4$

(iv)  $\log \gamma_{\pm} = 10^{-4}$

⇒  $\log \gamma_{\pm} = -A \cdot z_+ z_- \sqrt{I}$   
 $= -A \times 1 \times 1 \times \sqrt{I}$

(∵ 1:1 electrolyte  $I = C = 2M$ )

